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# JOURNAL

OF

## THE CHEMICAL SOCIETY.

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### TRANSACTIONS.

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1898. Vol. LXXIII.

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LONDON:  
GURNEY & JACKSON, 1, PATERNOSTER ROW.  
1898.

RICHARD CLAY AND SONS, LIMITED,  
LONDON AND BUNGAY. .

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TRANSACTIONS.

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I.—*Decomposition of Camphoric Acid by Fusion with Potash or Soda.*

By ARTHUR WILLIAM CROSSLEY and WILLIAM HENRY PERKIN, JUNR.

IN experimenting on the constitution of camphoric acid, one of the most characteristic properties which at once presents itself is the great stability of the acid, a property which makes it very difficult to attack by reagents and thus resolve it into smaller molecules.

It occurred to us, at an early stage in our experiments, that this difficulty might possibly be got over by the introduction of hydroxy-groups, as it seemed probable that a hydroxycamphoric acid would be more readily attacked than camphoric acid itself.

Some experiments which support this view have already been published by Rudzinski-Rudno (*Inaugural Dissertation Wurzburg*, 1879), who succeeded in oxidising hydroxycamphoric acid (camphanic acid) by means of potassium dichromate and sulphuric acid, the product being an acid to which he assigned the composition  $C_6H_{10}O_4$ , but this, as was afterwards shown by Brecht (*Annalen*, 145, 212), was in reality camphoronic acid. There can be no doubt that, under these conditions, camphanic acid is much more readily oxidised than camphoric acid.

Besides camphanic acid there has been another hydroxycamphoric acid described, namely, the so-called  $\alpha$ -hydroxycamphoric acid, which Hlasiwetz and Grabowski (*Annalen*, 1868, 145, 212) claim to have obtained by fusing camphoric acid with potash. It seemed probable to us that this acid, which is described as a thick syrup, and has therefore properties quite different from those of the beautifully crystalline camphanic acid, might yield important clues to the con-

stitution of camphoric acid if its behaviour towards reagents, and more especially to oxidising agents, was carefully studied and the results compared with those obtained with the isomeric camphanic acid. We therefore decided to prepare and examine this acid, and with this object carefully repeated the experiments of Hlasiwetz and Grabowski, without, however, being able to isolate even traces of an acid of the composition of a hydroxycamphoric acid.

Hlasiwetz and Grabowski fused 15 grams of camphoric acid with 45 grams of potash in a silver dish, acidified and extracted the product with ether; the residue, after distilling off the ether, was then distilled in steam to drive over the volatile fatty acids present. The distillate (which we now know to contain at least 10 different acids), was neutralised with ammonia, and the silver salt prepared and crystallised from water; on analysing this silver salt, numbers were obtained which led these chemists to the conclusion that the silver salt was silver butyrate or a mixture of this salt with silver isovalerate.

The acids which were not volatile with steam were dissolved in ammonia, the solution boiled with calcium chloride, and the insoluble precipitate, which consisted of calcium pimelate,\* removed by filtration; the filtrate from this salt was decomposed by dilute sulphuric acid, filtered from calcium sulphate, the filtrate decolorised with animal charcoal, and extracted with ether. On distilling off the ether, a syrup was left which was dissolved in water and precipitated by lead acetate; the caseous lead salt was then decomposed with hydrogen sulphide, and the syrupy mass obtained gave, on analysis, numbers which, as these authors state, did not agree very well together, but nevertheless pointed to the formula  $C_{10}H_{16}O_5$ , that of a hydroxycamphoric acid. This acid was not altered by fusion with potash, but on distillation it gave a small quantity of camphoric acid, and we have no doubt that it was a mixture of several substances.

During the course of numerous preliminary experiments on the fusion of camphoric acid with potash, we found that the decomposition was much more complex than Hlasiwetz and Grabowski supposed, and as there was every prospect that the careful and systematic examination of the substances formed might give some clue to the constitution of camphoric acid, we decided to devote our attention to the study of this reaction.

Our first experiments were made with the quantities and under the conditions recommended by Hlasiwetz and Grabowski, but subsequently we found that the same results were obtained whether we fused 25, 50, or 100 grams of camphoric acid in one operation, and after having fused in this way about 2 kilos. of camphoric acid, we devoted some

\* The "pimelic acid" referred to repeatedly in this research is always isopropylsuccinic acid,  $CH(CH_3)_2 \cdot CH(COOH) \cdot CH_2 \cdot COOH$ .



months to the investigation of the products which had been formed. However, as the work progressed, and we gradually became thoroughly aware of the complicated nature of the mixture of substances with which we had to deal, it was at once evident that the investigation could not be satisfactorily carried out unless very large quantities of material were employed.

But then serious difficulties presented themselves, for the ordinary laboratory apparatus would not permit of sufficiently large quantities being handled conveniently ; ultimately, however, through the great kindness of Mr. Ivan Levinstein, these obstacles were overcome, and we were enabled to fuse as much as 500 grams of camphoric acid in one operation. Mr. Levinstein placed a large room in his works at Crumpsall, near Manchester, at our entire disposal, and after having consulted with us, fitted up all the special apparatus which was necessary for carrying out our experiments on the large scale. We beg to take this opportunity of thanking Mr. Levinstein for his great kindness and liberality, without which it would have been impossible to have carried out this work, and we also thank him for the interest which he took in the subsequent progress of our research.

In our preliminary investigations, we had found that when caustic soda was used instead of caustic potash, the nature of the products of decomposition seemed to be in many respects different ; it was therefore thought advisable to try the fusion of camphoric acid with caustic soda on the large scale, and the subsequent results show that this decision was thoroughly warranted.

#### *I.—The Substances Formed when Camphoric Acid is Fused with Potash.*

The method adopted in carrying out the fusion is described in detail in the experimental part of this paper, and we therefore propose only to give here a brief account of the way the melts were worked up and the nature of the products obtained.

The melts from 5 kilos. of camphoric acid were dissolved in water, acidified, and distilled with steam until the condensed water had only the faintest acid reaction ; the distillate was neutralised, evaporated down to a small bulk, acidified, and extracted with ether, when about 2·3 kilos. of oily fatty acids were obtained.

The residue in the still was filtered from the potassium sulphate which crystallised out on cooling, neutralised with caustic soda, and evaporated, when the concentrated liquor, on standing, deposited a large quantity of the sulphates of sodium and potassium mixed with a considerable amount of organic salts. These crystals were collected, dissolved in water, acidified, and extracted with ether, and in this way 510 grams of a pale yellow oil (A) was obtained. From the mother

liquor from the crystals, 346 grams of a dark yellow oil (B) was subsequently extracted.

The 2·3 kilos. of fatty acids were submitted to most careful fractional distillation in specially constructed apparatus, and ultimately the following acids were isolated and identified, not only by the boiling points and analysis of the acids themselves and of their silver salts, but also by the preparation of their anilides, and in some cases of their paratoluidides.

Name.	Formula.	Boiling point.*
Acetic acid.....	$\text{CH}_3\cdot\text{COOH}$	118°
Propionic acid .....	$\text{CH}_3\cdot\text{CH}_2\cdot\text{COOH}$	141
Isobutyric acid .....	$\text{CH}(\text{CH}_3)_2\cdot\text{COOH}$	154
Isovaleric acid .....	$\text{CH}(\text{CH}_3)_2\cdot\text{CH}_2\cdot\text{COOH}$	174
Methylisopropylacetic acid .....	$\text{CH}(\text{CH}_3)_2\cdot\text{CH}(\text{CH}_3)\cdot\text{COOH}$	190

In view of the fact that it is now generally assumed that camphoric acid contains the group  $(\text{CH}_3)_2\text{C}\cdot\text{C}(\text{CH}_3)-$ , it is interesting to note the repeated occurrence of the isopropyl group,  $(\text{CH}_3)_2\text{CH}-$ , in the above acids, and of the whole group,  $(\text{CH}_3)_2\text{CH}\cdot\text{CH}(\text{CH}_3)-$ , in the last acid in the table.

The acids distilling above 190° were very difficult to work with, but by converting the portion boiling at 206—212° into the mixed anilides, and crystallising these from light petroleum, a very sparingly soluble, well characterised anilide was obtained which melted at 105°, and on analysis gave numbers agreeing with the formula  $\text{C}_6\text{H}_{13}\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_5$ . The acid obtained by the hydrolysis of this pure anilide, boiled constantly at 209—210°, and had the composition  $\text{C}_6\text{H}_{13}\cdot\text{COOH}$ , but, apparently, it is not identical with any of the acids of this formula which have hitherto been investigated. Without having any definite proof to offer, we think it likely that this acid may be *βββ-dimethylethylpropionic acid*,  $\text{CH}_3\cdot\text{CH}_2\cdot\text{C}(\text{CH}_3)_2\cdot\text{CH}_2\cdot\text{COOH}$ , and we are endeavouring to prepare this acid synthetically with the view of deciding this point.

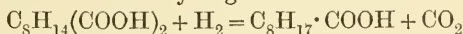
The acids boiling above 220° were submitted to systematic, repeated fractional distillation, using small columns made for us by Geissler especially for this purpose; by this means, we were able to isolate two acids which boiled remarkably constantly at 230—232° and 240—242° respectively.

The acid boiling at 230—232°, on analysis, gave numbers agreeing

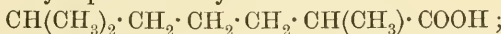
\* The numbers given in this column are the true boiling points of the acids; the fractions obtained and actually examined and analysed are given in the experimental part of this paper.

well with the formula  $C_7H_{15} \cdot COOH$ , and although it may contain small quantities of the homologues of lower and higher boiling point, we think it improbable, and are also disinclined to believe that it consists of isomeric acids of the above formula. This acid, on oxidation with permanganate, yields, besides fatty acids of low boiling point (consisting apparently of acetic and propionic acids), succinic acid and  $\alpha$ -methylglutaric acid,  $CH_3 \cdot CH(COOH) \cdot CH_2 \cdot CH_2 \cdot COOH$ , and we have suggested the formula  $(CH_3)_2CH \cdot CH(CH_3) \cdot CH_2 \cdot CH_2 \cdot COOH$  as probably representing its constitution.

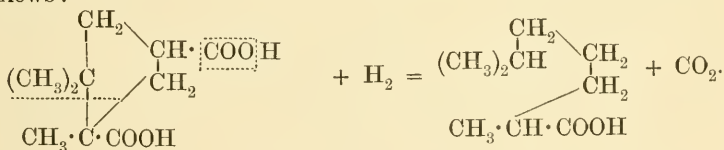
The acid boiling at  $240-242^\circ$  is a very interesting compound, since on analysis it gives numbers agreeing with the formula  $C_8H_{17} \cdot COOH$ , and this is confirmed by the analysis of the silver salt,  $C_8H_{17} \cdot COOAg$ . Such an acid would be derived from camphoric acid by the elimination of carbonic anhydride, and splitting of the ring by the addition of two hydrogen atoms.



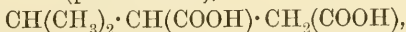
This acid, on oxidation, yields an acid which, from its properties, is evidently  $\alpha$ -methylglutaric acid, and its constitution, therefore, is in all probability represented by the formula



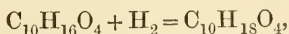
this formula could easily be derived from camphoric acid, on the assumption that it has the constitution represented here,\* as follows:



The oily acids A and B contained, besides large quantities of isopropylsuccinic acid (pimelic acid),



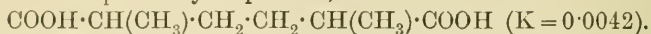
a very interesting dibasic acid of the composition  $C_{10}H_{18}O_4$ , which crystallises well, melts at  $106^\circ$ , and gives a silver salt of the composition  $C_8H_{16}(COOAg)_2$ . This acid, which must have been formed by the reduction of camphoric acid at the high temperature of the melt, with consequent splitting of the ring



we have named *dihydrocamphoric acid*. It differs in nearly all its properties from camphoric acid, and has a much higher dissociation constant,

\* This formula for camphoric acid is used in this paper because, from results obtained by one of us in the examination of sulphocamphylic acid, and which are shortly to be communicated to the Society, it seems the most probable.

the value found by Dr. Ewan ( $K=0.00415$ ) being nearly twice as great as that of camphoric acid ( $K=0.0025$ ), and almost identical with that of  $\alpha\alpha_1$ -dimethyladipic acid,

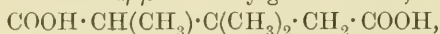


When treated with acetic anhydride, this acid is converted into a liquid which, from the analysis, appears to be the anhydride, and this, when heated, is decomposed in a remarkable manner into carbonic anhydride and a ketone of the formula  $\text{C}_9\text{H}_{16}\text{O}$



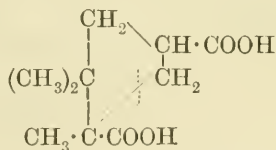
This new ketone, which we have called *dihydrocamphoketone*, is a liquid which boils at  $180-181^\circ$ , and has a most penetrating odour of peppermint; it is well characterised by forming a beautifully crystalline *semicarbazone* which melts at  $202-203^\circ$ .

It is readily oxidised by boiling with dilute nitric acid, with formation of succinic acid, oxalic acid, and an acid,  $\text{C}_8\text{H}_{14}\text{O}_4$ , which melts at  $94^\circ$ , and gives an anilic acid melting at  $159^\circ$ . These properties indicate that this acid is  $\alpha\beta\beta$ -trimethylglutaric acid,

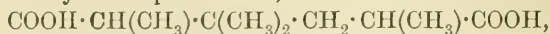


which Balbiano (*Berichte*, 1895, 28, 1507) obtained from camphoric acid, and which, he states, melts at  $94-95^\circ$  and gives an anilic acid melting at  $159^\circ$ .

Starting from the constitution of camphoric acid which was suggested on p. 5, namely,



there seems to be only one formula which satisfactorily explains the reactions of dihydrocamphoric acid, and that is

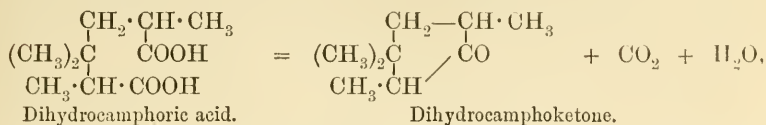


a formula obtained by adding on two atoms of hydrogen at the point marked  $\vdots$  in the formula for camphoric acid given above; this represents the substance as  $\alpha\alpha_1\beta\beta$ -tetramethyladipic acid, and experiments are now being carried out with the object of preparing this acid synthetically, and comparing its properties with those of dihydrocamphoric acid.

It has already been stated that the constant for the electrical conductivity of this acid ( $K=0.00415$ ) agrees very closely with that of  $\alpha\alpha_1$ -dimethyladipic acid ( $K=0.0042$ ), and this fact, taken in conjunction with the great readiness with which the acid loses carbonic anhydride with formation of the cyclic ketone, *dihydrocamphoketone* (compare especially J. Bredt and M. v. Rosenberg, *Annalen*, 1896, 289, 1-14,

and J. Wislicenus, *ibid.*, 1893, 275, 309), seems to us to show conclusively that the acid is a derivative of adipic acid.

The formation of dihydrocamphoketone would then be expressed thus



and this view of the constitution of dihydrocamphoketone is a very probable one, since the formula readily explains the formation of  $\alpha\beta\gamma$ -trimethylglutaric acid by the oxidation of the ketone.

Dihydrocamphoketone is very similar, in many of its properties, to camphorophorone, the ketone which is formed when the calcium salt of camphoric acid is distilled, and which boils at 200—205° and has a penetrating odour of peppermint. The latter ketone, on oxidation, yields  $\alpha$ -methylglutaric acid, formic acid, and acetic acid (Königs, Eppens, *Berichte*, 25, 266), a decomposition which has led Brecht (*loc. cit.*) to

propose the formula,  $\begin{array}{c} \text{CH}_2 \cdot \text{C}[\text{C}(\text{CH}_3)_2] \\ | \\ \text{CH}_2 - \text{CH}(\text{CH}_3) \end{array} > \text{CO}$ , for camphorophorone. If this formula should prove correct, it is probable that, in spite of the similarity in properties, there is no close connection between this substance and dihydrocamphoketone.

## II. The Substances formed when Camphoric Acid is Fused with Soda.

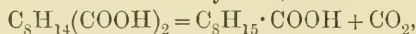
The fusion of 4 kilos. of camphoric acid with soda was carried out under the same conditions and in the same apparatus as was used in the experiments with caustic potash, and the melts were worked up in the first instance in a very similar manner to the potash melts. The amount of acids volatile with steam in this case was very much less than that obtained from the potash melts, 5 kilos. of camphoric acid fused with potash yielded 2.3 kilos. of volatile acids, whereas from 4 kilos. fused with soda only 715 grams were obtained. A great difference was also noticed in the composition of the acids from the two experiments, and this is well brought out by tables which have been introduced into the experimental part of this research (p. 33). The constitution of the various acids which were obtained by fractionating the 715 grams from the soda melts was very carefully investigated, in order to determine whether any difference could be noted in the nature of these acids as compared with those from the potash melts, but this does not appear to be the case except in the highest fraction of all.

In fractioning the acids from the potash melts, a small quantity of an oil was obtained boiling at 240—242°, which, on analysis, was

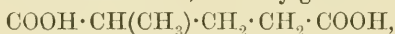


found to consist for the most part of a saturated acid of the formula  $C_8H_{17} \cdot COOH$ . From the soda melts, a comparatively much larger quantity of an acid of the same boiling point was obtained, which, however, on repeated analysis, was found not to be identical with the acid  $C_8H_{17} \cdot COOH$ , but to contain two atoms of hydrogen less, and to be an unsaturated acid of the formula  $C_8H_{15} \cdot COOH$ .

This acid, which apparently had been formed from camphoric acid by the elimination of carbonic anhydride,



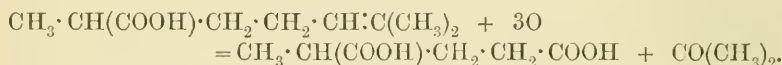
decolorises permanganate instantly in the cold, and is converted into a *dibromo-acid* of the formula  $C_8H_{15}Br_2 \cdot COOH$ , by treatment with bromine. On oxidation, first with permanganate and then with chromic acid, it yielded, besides acetic acid,  $\alpha$ -methylglutaric acid,



and we therefore suggest that its constitution may probably be expressed by the formula

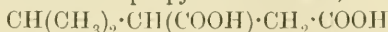


a formula which it will be seen can readily be deduced from the constitution of camphoric acid adopted in this paper, and from the suggested constitution of the acid  $C_8H_{17} \cdot COOH$  (p. 5), with which, no doubt, it is closely allied. This formula is rendered probable from the fact that a distinct odour of acetone was noticed during the oxidation with chromic acid; and the oxidation may then be assumed to have taken place in the following way:



The acetone would then, on further oxidation, yield the acetic acid which was found among the products. It should be mentioned that a careful examination of the acids boiling at  $240-242^\circ$  from the potash and soda melts has shown that the products, in both cases, contain the saturated acid  $C_8H_{17} \cdot COOH$  and the unsaturated acid  $C_8H_{15} \cdot COOH$ , traces of the former being found in the soda melts and traces of the latter in the potash melts; this difference is doubtless due to the well-known fact that potash when fused with organic substances exercises a more powerful reducing action than soda.

The examination of the acids produced on fusing camphoric acid with soda, and which were not volatile in steam, has given most interesting results. These acids, which weighed 700 grams, contained, besides considerable quantities of isopropylsuccinic acid,



(pimelic acid), and some camphoric acid, small quantities of two new acids, one crystalline and the other a syrup; these were separated

from the pimelic acid and camphoric acid only with great difficulty, and by methods which are described in detail in this paper.

The crystalline acid which melts at 119—120°, on repeated analysis, gave numbers which showed that it was a dibasic acid of the formula  $C_8H_{14}(COOH)_2$ , that it was, in fact, a new isomeride of camphoric acid.

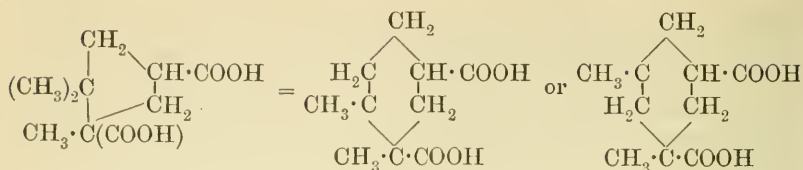
This acid which we have called *pseudo-camphoric acid*, gives well-defined salts of which the *silver* salt,  $C_8H_{14}(COOAg)_2$ , was repeatedly analysed. It yields also a crystalline *anhydride*,  $C_8H_{14}\begin{smallmatrix} \diagup CO \\ \diagdown CO \end{smallmatrix} O$ , which melts at 52—53°, and an anilic acid,  $COOH \cdot C_8H_{14} \cdot CO \cdot NH \cdot C_6H_5$ , melting at 208°. Pseudocamphoric acid does not decolorise alkaline permanganate except on long standing, and it is therefore, like camphoric acid, saturated, but it differs from the latter in that when treated with sulphuric acid, it does not evolve carbon monoxide and yield a sulphonic acid of the nature of sulphocamphylic acid.

Before Aschan's classical researches on the camphoric acids had been published (*Berichte*, 27, 2001, *Chemisches Centralblatt*, 1895, 51, 967), thirteen isomeric forms of these acids had been described: Aschan, however, showed that in reality there were only six modifications namely, the four active acids *d*- and *l*-camphoric acid and *d*- and *l*-isocamphoric acid, and the two inactive racemoid forms, *i*-camphoric acid and *i*-isocamphoric acid. The active camphoric acids melt at 187° and *i*-camphoric acid at 202—203°, the active isocamphoric acids have lower melting points, namely, 171—172° and *i*-isocamphoric acid melts at 191°. The camphoric acids belong to the *cis*-form and yield anhydrides, whereas the isocamphoric acids which are *trans*-modifications do not do so.

These are the only modifications possible on the assumption that camphoric acid has the formula suggested by Bredt or the formula adopted in this paper.

It will be seen that our *pseudocamphoric acid* is quite different in its properties from any of the above acids; moreover, that it is not a mixture of a camphoric acid and an isocamphoric acid, such as has been, in previous cases, found to melt at about 130°, and therefore described as new, is shown by the fact that our acid, when treated with acetyl chloride according to Aschan's directions, remains unaltered, whereas such a mixture would yield the anhydride of the camphoric acid, whilst the isocamphoric acid remained unchanged.

It seems very probable that, in the formation of pseudocamphoric acid from camphoric acid, the 5 ring in the latter acid has been converted into a 6 ring by the introduction of one of the methyl groups of the complex  $(CH_3)_2C=$  thus.



These formulæ represent pseudocamphoric acid as a derivative of hexahydrophthalic acid on the one hand, and on the other as a substituted glutaric acid, and either view agrees well with the properties of the acid, and especially with the fact that it yields a well characterised anhydride and anilic acid.

The syrupy acid mentioned on p. 8 as having been obtained from that portion of the acids not volatile with steam, is a substance having very interesting properties. It is a very viscid, colourless syrup which distils remarkably constantly at 254—257° (50 mm.), and, on examination, has been found to consist of an acid of the formula  $\text{C}_9\text{H}_{16}\text{O}_4$  very soluble in water, mixed with very small quantities of an oil insoluble in water, properties which make it easy to separate the two.

The acid  $\text{C}_9\text{H}_{16}\text{O}_4$  differs from all the other substances described in this paper in that, in spite of its high molecular weight, it is unusually soluble, in fact almost miscible with water. It is a dibasic acid which yields a *silver* salt,  $\text{C}_7\text{H}_{14}(\text{COOAg})_2$ , and although it distils almost without change, that is, without forming an anhydride, it does yield an anhydride,  $\text{C}_7\text{H}_{14} \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{CO} \end{smallmatrix} \text{O}$ , boiling at 185—190° (35 mm.) when digested with acetic anhydride. We have not, so far, been able to obtain any clue to the nature of this acid.

This research was commenced in 1893 in the laboratories of Owens College, and since 1895 it has been carried on uninterruptedly both in Owens College and in the chemical laboratory of St. Thomas's Hospital, and we wish to express our hearty thanks to Messrs. W. H. Bentley, G. Haworth, J. L. Heinke, F. H. Lees, and others for valuable help in carrying out this difficult investigation.

## EXPERIMENTAL.

### FUSION OF CAMPHORIC ACID WITH CAUSTIC POTASH.

*Description of the Melting.*—Five kilos. of camphoric acid were treated in the following manner. Five hundred grains of camphoric acid were mixed with 4 kilos. of caustic potash containing 85 per cent. KOH in a large iron pot, and the whole well moistened with water; the pot was then rapidly heated with two very large Fletcher burners, the contents



being meanwhile well stirred. As the temperature gradually rose, the mass assumed a pasty consistency, and at about  $170^{\circ}$  to  $180^{\circ}$  bubbles appeared round the edge of the melt, increasing in number with the rise in temperature; water was given off and a small amount of a light coloured scum formed on the surface. At  $250^{\circ}$ , the melt set to a hard mass and could only be stirred with difficulty; great care was required at this stage to prevent charring. On continuing to heat, the melt again became quite liquid at about  $300^{\circ}$ , and just above  $360^{\circ}$  began to give off large quantities of hydrogen, at the same time a penetrating aromatic odour somewhat resembling that of menthol was observed. The evolution of hydrogen continued for from 2— $2\frac{1}{2}$  hours, and the whole operation lasted from 3— $3\frac{1}{2}$  hours. As soon as hydrogen ceased to be evolved, the melt was poured on to shallow iron trays and allowed to cool, when it soon solidified to a hard, brittle cake of a greenish colour.

*Working up of the Product.*—When cold, the melt was broken up and placed in a lead-lined iron vessel (specially fitted up for steam distillation), a large amount of water added, and steam passed through until the whole was dissolved. The lid of the vessel was then fastened down, and through a tap in the lid a quantity of 33 per cent. sulphuric acid was run in somewhat more than sufficient (this was calculated from experiments made with small samples of the different melts) to combine with the caustic potash used, and the whole submitted to steam distillation until the condensed water had only a very slight acid reaction. The acid distillate was neutralised with caustic soda and evaporated to dryness.

By this means, 4 kilos. of sodium salts were obtained, which were dissolved in the least possible quantity of water, strongly acidified with hydrochloric acid and extracted with ether; the ethereal solution was dried over calcium chloride and the ether evaporated; the residue weighed 2.3 kilos. and was treated in the manner described in detail on page 12.

*Residue from the Steam Distillation.*—The residue from the distillation with steam, on cooling, deposited large quantities of potassium sulphate; this was filtered off, and the filtrate neutralised with caustic soda and evaporated to about one-third its bulk in large, flat copper pans, heated by steam. The salts which separated from this concentrated liquor contained much organic matter, and on treatment with hydrochloric acid and ether in the manner just described, yielded 510 grams of a pale yellow oil (A).

Lastly, the filtrate from the above salt was evaporated to dryness; at a later date, this solid residue was dissolved in water, strongly acidified with hydrochloric acid, and treated with ether as above, when 346 grams of a dark yellow oil (B) was obtained.

The process adopted in working up the oils (A) and (B) is described on pages 22 and 23.

*Volatile Acids formed by the Fusion of Camphoric Acid with Potash.*

The 2·3 kilos. of crude acids which had been volatilised with steam (p. 11) were now carefully fractionated, using a column, with the following results.

Fraction.	Weight in grams.
50—100°	296
100—125	663
125—135	515
135—150	387
above 150	325

The fraction 50—100° contained water and ether; the ethereal solution separated from the water was carefully dried over anhydrous sodium sulphate; the fractions 100—125°, 125—135°, and 135—150° were also carefully dried over sodium sulphate, and the whole was then repeatedly distilled, the acids, after each distillation, being again dried over anhydrous sodium sulphate. The appended table gives the result of this treatment.

Fraction.	Weight in grams after 2nd distillation.	Weight in grams after 3rd distillation.	Weight in grams after 4th distillation.
50—100°	13	—	—
100—125	501	689	701
125—135	Not distilled	310	330
135—150	„	360	285
above 150			20

The acids boiling above 150° gave the following results on fractionation.

Fraction.	Weight in grams after 1st distillation.	Weight in grams after 2nd distillation.
below 150°	2	15
150—160	12	58
160—170	68	40
170—180	59	33
180—190	41	36
190—200	42	31
200—210	42	42
210—220	43	48
220—230	33	30
230—240	22	14
above 240	22	32

From the acids boiling above  $240^{\circ}$ , a small amount of solid matter crystallised out on standing, which, when separated from the liquid and dried, was found to have a melting point of  $114^{\circ}$ , corresponding with that of pimelic acid (isopropylsuccinic acid). The presence of this acid could only be accounted for by assuming that it was to some extent volatile with steam, and, in order to test this supposition, the following experiment was made.

Five grams of pimelic anhydride were dissolved in caustic soda, acidified with sulphuric acid, and steam distilled for  $1\frac{3}{4}$  hours. The distillate, after being neutralised with caustic soda, evaporated, acidified with sulphuric acid, extracted with ether, &c., gave 0.2 gram of a crystalline solid having a melting point of  $114^{\circ}$ , which is that of pimelic acid. This shows that pimelic acid is to some extent carried over during steam distillation.

It was thought that a separation of pimelic acid from the fatty acids might be effected, if the ammonium salts were distilled with steam. The salts of the fatty acids would by this means be dissociated into ammonia and the free acids which would distil over, whereas the ammonium salt of pimelic acid might be expected to remain undecomposed.

On making a blank experiment in this way with 20 grams of pimelic anhydride, it was found that the ammonium salt of pimelic acid is not decomposed during steam distillation.

In order to test this method of separation further, a considerable amount of acids from which a small quantity of the crystalline substance, melting at  $114^{\circ}$ , had been obtained, was dissolved in ammonia and steam distilled until no more acid came over with the condensed water. The ethereal extract from the acidified residue left in the retort solidified completely on standing, and the crystals melted at  $114^{\circ}$  (pimelic acid). These experiments showed that the acids boiling above  $150^{\circ}$  must contain pimelic acid, and as it was necessary to get rid of this substance, the whole of the fatty acids boiling above this temperature was dissolved in ammonia and steam distilled. The total amount of crude pimelic acid obtained from the residue was about 45 grams. During the distillation, the first portion which passed over was strongly alkaline (from the presence of ammonia) and from this liquid a small amount of an oil separated (about 2 grams); this was extracted with ether, but the quantity was too small to allow of its nature being investigated. The combined distillates from the steam distillation were neutralised with caustic soda, evaporated, acidified and treated with ether, &c., as described on p. 11, and fractionated.

Fraction.	Weight in grams before the ammonium salt purification.	Weight in grams after the ammonium salt purification.	Weight in grams of acid from residue after distillation.
150—160°	58	31	20
160—170	40	25	
170—180	33	25	
180—190	36	35	
190—200	31	20	
200—210	42	43	25
210—220	48	32	
220—230	30	54	
230—240	14	20	
above 240	32	6	

*The Fraction 100—125° contains Acetic Acid, CH<sub>3</sub>·COOH.*—In order to thoroughly dry this fraction, it was mixed with an equal volume of concentrated sulphuric acid, allowed to stand for 24 hours, and then distilled; this operation was repeated four times, and finally, after several fractional distillations, a considerable quantity of pure acetic acid was isolated which solidified on cooling with ice. The silver salt prepared from this, after recrystallisation from water, gave the following result on analysis.

0·1996, on ignition, gave 0·1290 Ag. Ag = 64·62.

CH<sub>3</sub>COOAg requires Ag = 64·67 per cent.

The acid was further characterised by converting it into ethylic acetate and acetanilide.

*The Fraction 135—150° contains Propionic Acid, CH<sub>3</sub>·CH<sub>2</sub>·COOH.*—After drying with sulphuric acid and repeated very careful fractional distillation, a portion was isolated which boiled constantly at 140°, and, on analysis, was shown to be propionic acid.

0·1628 gave 0·2909 CO<sub>2</sub> and 0·1224 H<sub>2</sub>O. C = 48·72; H = 8·35.

CH<sub>3</sub>·CH<sub>2</sub>·COOH requires C = 48·64; H = 8·10 per cent.

The silver salt was also analysed.

I. 0·1540, on ignition, gave 0·0918 Ag. Ag = 59·61.

II. 0·2689 „ „ „ 0·1602 Ag. Ag = 59·57.

0·2689 gave 0·1942 CO<sub>2</sub> and 0·0658 H<sub>2</sub>O. C = 19·70; H = 2·71.

C<sub>3</sub>H<sub>5</sub>O<sub>2</sub>Ag requires Ag = 59·66; C = 19·89; H = 2·76 per cent.

*The Fraction 150—160° contains Isobutyric Acid.*—Hlasiwetz and Grabowski considered that the acid formed by the action of fused potash on camphoric acid consisted of butyric acid. We have, however, failed to substantiate this statement, as we have not succeeded in isolating any butyric acid, although, on the other hand, we find that *iso*-butyric acid is formed in considerable quantities during the fusion.

As the boiling points of the two butyric acids are near to one another (normal acid,  $163^{\circ}$ ; *iso*-acid,  $150^{\circ}$ ) it was feared that, if both were present, distillation alone would not separate them. Wechsler's\* method (*Monatshefte*, July, 1893, 462) was therefore resorted to.

For this purpose, the whole of the fraction  $150\text{--}160^{\circ}$  was neutralised with standard caustic soda, one-third of the amount of standard sulphuric acid necessary to neutralise the soda was added, and the mixture steam distilled until the distillate was no longer acid. According to Wechsler, under these conditions, the acid of higher boiling point comes over first; so that the distillate should contain butyric acid, if any were present. An analysis of the fraction  $160\text{--}166^{\circ}$  of the acids obtained from the distillate gave the following numbers.

0.1918 gave 0.3980  $\text{CO}_2$  and 0.1631  $\text{H}_2\text{O}$ .  $\text{C} = 56.62$ ;  $\text{H} = 9.43$ .  
 $\text{C}_4\text{H}_8\text{O}_2$  requires  $\text{C} = 54.54$ ;  $\text{H} = 9.09$ .  $\text{C}_5\text{H}_{10}\text{O}_2$  requires  $\text{C} = 58.82$ ;  $\text{H} = 9.80\%$ .

Evidently the substance is a mixture of probably isobutyric acid (or butyric acid) and isovaleric acid.

To the residue of the distillation, another portion of the standard acid, equal to one-third of the soda solution originally used, was added, and the whole again distilled in steam. The distillate was heated with excess of calcium carbonate, filtered, and the clear filtrate concentrated on the water bath, when, on cooling, well-defined, white, feathery crystals separated. A portion of the clear mother liquor, which had a syrupy consistency, was heated at  $100^{\circ}$  in a closed tube, but only a minute quantity of solid matter was precipitated, showing that not more than a trace of the calcium salt of normal butyric acid could have been present.

The acid, recovered from the calcium salt in the usual way, by acidifying and extracting with ether, was submitted to fractional distillation, and the portion boiling between  $152^{\circ}$  and  $153^{\circ}$  was analysed.

0.1561 gave 0.3089  $\text{CO}_2$  and 0.1250  $\text{H}_2\text{O}$ .  $\text{C} = 53.98$ ;  $\text{H} = 8.9$ .

$\text{C}_4\text{H}_8\text{O}_2$  requires  $\text{C} = 54.54$ ;  $\text{H} = 9.09$  per cent.

The calcium salt prepared from this acid was also analysed.

0.1264, dried at  $100^{\circ}$ , gave 0.0828  $\text{CaSO}_4$ .  $\text{Ca} = 18.98$ .

0.1708 of the air-dried salt lost 0.0440  $\text{H}_2\text{O}$  at  $155^{\circ}$ .  $\text{H}_2\text{O} = 25.76$ .

$(\text{C}_4\text{H}_7\text{O}_2)_2\text{Ca}$  requires  $\text{Ca} = 18.69$  per cent.

$(\text{C}_4\text{H}_7\text{O}_2)_2\text{Ca}, 4\text{H}_2\text{O}$  requires  $\text{H}_2\text{O} = 25.17$ .  $(\text{C}_4\text{H}_7\text{O}_2)_2\text{Ca}, 5\text{H}_2\text{O}$  requires  $\text{H}_2\text{O} = 29.60$  per cent.

This determination of the water of crystallisation agrees well with that of the calcium salt obtained from the soda melts; but according

\* This method, although in some cases valuable, is not so trustworthy as might be supposed from the description given by Wechsler, as detailed experiments, carried out by one of us, show (*Trans.*, 1897, 71, 580).



to Chancel and Parmentier (*Compt. rend.*, 1887, 104, 477) calcium isobutyrate contains  $5\text{H}_2\text{O}$ . An examination of the calcium salt prepared from pure isobutyric acid showed that, if left exposed to the air, it loses some of its water of crystallisation; this accounts for the numbers obtained in the above analysis being low.

These experiments prove conclusively that isobutyric acid is one of the acids formed during the fusion of camphoric acid with caustic potash.

*The Fraction 170—180° contains Isovaleric Acid,*



—The very disagreeable smelling oily acids boiling within these limits were repeatedly fractionated, when a considerable quantity was obtained boiling at  $175\text{—}180^\circ$ ; the product, on analysis, gave the following result.

0.1207 gave 0.2592  $\text{CO}_2$  and 0.1092  $\text{H}_2\text{O}$ .  $\text{C} = 58.57$ ;  $\text{H} = 10.04$ .

$\text{C}_5\text{H}_{10}\text{O}_2$  requires  $\text{C} = 58.82$ ;  $\text{H} = 9.80$  per cent.

The whole of this fraction was converted into the anilide which was purified by crystallisation from light petroleum (b. p.  $100\text{—}120^\circ$ ). It formed shining, white needles which melted at  $109.5\text{—}110.5^\circ$ .

I. 0.1141 gave 8.1 c.c. moist nitrogen at  $12^\circ$  and 752 mm.  $\text{N} = 8.33$ .

II. 0.1154 „ 7.9 „ „ 13.5° „ 769 mm.  $\text{N} = 8.16$ .

$\text{C}_{11}\text{H}_{15}\text{NO}$  requires  $\text{N} = 7.91$  per cent.

According to Chiozza (*Ann.*, 1852, 84, 109), the melting point of iso-valeranilide is  $115^\circ$ ; whilst Schmidt and Sachtleben (*Ann.*, 1878, 193, 102) state that the anilide prepared from synthetical isobutylformic (isopropylacetic) acid melts at  $100^\circ$ .

In order to test these statements, isopropylacetic acid was prepared from ethylic isopropylmalonate. This ethereal salt after careful fractionation was hydrolysed with alcoholic potash, the dibasic acid distilled to eliminate carbon dioxide, and the distillate fractionated. A portion of the pure acid boiling at  $175^\circ$  was converted into the anilide, which, after repeated recrystallisation from light petroleum, melted at  $109\text{—}111^\circ$ ; this agrees with the melting point of the acid prepared from the fusion of camphoric acid with caustic potash, proving that the acid described above is isovaleric acid.

*The Fraction 180—200° contains Methylisopropylacetic Acid,*



—The fraction of the fatty acids boiling between  $180^\circ$  and  $200^\circ$  (about 70 grams) was 12 times very carefully fractionated, the following fractions being ultimately obtained.

180—183° = 5 grams

189—192° = 15 grams

183—186° = 8 „

192—195° = 11 „

186—189° = 14 „

195—198° = 7 „

The fraction 186—192°, which weighed 29 grams, was converted into the anilide in the usual way, and this, on standing for some days in an ice chest over sulphuric acid in a vacuum desiccator, deposited crystals which, after being left in contact with porous porcelain for a fortnight, were purified by repeated crystallisation from dilute methylic alcohol. The anilide thus obtained melted sharply at 75°, and gave the following numbers on analysis.

0.1608 gave 10.4 c.c. moist nitrogen at 15° and 750 mm.  $N = 7.47$ .

$C_5H_{11} \cdot CO \cdot NH \cdot C_6H_5$  requires  $N = 7.33$  per cent.

This pure anilide was digested with concentrated hydrochloric acid, and the regenerated acid, after extraction with ether and drying over calcium chloride, was distilled, when the whole passed over at 189—191° (766 mm.) and gave, on analysis, the following numbers.

0.1451 gave 0.3288  $CO_2$  and 0.1338  $H_2O$ .  $C = 61.82$ ;  $H = 10.24$ .

$C_5H_{11} \cdot COOH$  requires  $C = 62.07$ ;  $H = 10.34$  per cent.

The silver salt prepared from the ammonium salt by precipitation, is amorphous and insoluble.

0.1340 gave, on ignition, 0.0645 Ag.  $Ag = 48.13$

$C_5H_{11} \cdot COOAg$  requires  $Ag = 48.43$  per cent.

In order to further characterise this acid, it was converted into the paratoluidide,  $C_5H_{11} \cdot CO \cdot NH \cdot C_6H_4 \cdot CH_3$ , by treating the acid chloride with paratoluidine. As the crude product of the action did not crystallise readily, it was ground up for some days successively with small quantities of dilute sodium carbonate solution, and dilute hydrochloric acid; it ultimately became quite hard, and was then purified by recrystallisation from light petroleum (b. p. 60—80°) from which it separated in colourless needles melting at 103—104°.

0.1522 gave 8.8 c.c. moist nitrogen at 14° and 752 mm.  $N = 6.73$ .

$C_5H_{11} \cdot CO \cdot NH \cdot C_6H_4 \cdot CH_3$  requires  $N = 6.83$  per cent.

As the boiling point of this acid coincides exactly with that of methylisopropylacetic acid ( $\alpha\beta\beta$ -trimethylpropionic acid) which one of us had previously prepared (Trans., 1896, 69, 1476), it seemed probable that the two acids might be identical. In order to test this, synthetic methylisopropylacetic acid boiling at 189—190° was converted into the anilide and paratoluidide, which were found to be identical in every respect with those prepared from the acid described above. The acid obtained by the fusion of camphoric acid with potash, and boiling at 189—191°, is therefore methylisopropylacetic acid.

*Examination of the Acids Boiling at 200—220°.*

It will be seen from the table on page 14 that no less than 75 grams of acid of the fraction distilling between 200 and 220° had been obtained; and it seemed probable that a careful examination of it might furnish very interesting results. Accordingly, the mixture was very carefully fractionated (12 times) with the following results.

200—203° = 6 grams	209—212° = 19 grams
203—206 = 10 „	212—215 = 9 „
206—209 = 21 „	215—218 = 4 „

The fraction 206—212°, converted into the acid chloride in the usual way, distilled entirely between 115° and 120° (200 mm.). The oily anilide prepared from this, after being kept for some days at 0°, deposited a semi-solid mass of crystals. This, when placed on porous porcelain, left an almost colourless crystalline cake, which was purified by recrystallisation from light petroleum (b. p. 60—90°); in this way, a very sparingly soluble anilide was easily isolated in a beautifully crystalline condition, and melting sharply at 105—105·5°.

0·2146 gave 13·2 c.c. moist nitrogen at 20° and 754 mm.  $N = 6·98$ .

$C_6H_{13} \cdot CO \cdot NH \cdot C_6H_5$  requires  $N = 6·83$  per cent.

The anilide was now decomposed by digestion with strong hydrochloric acid in a reflux apparatus for about two days; the oily acid, extracted with pure ether in the usual way, was purified by fractionation, when almost the whole distilled at 209—210° as a colourless oil.

0·1494 gave 0·3521  $CO_2$  and 0·1425  $H_2O$ .  $C = 64·27$ ;  $H = 10·60$ .

0·1384 „ 0·3269  $CO_2$  „ 0·1338  $H_2O$ .  $C = 64·42$ ;  $H = 10·74$ .

0·1522 „ 0·3604  $CO_2$  „ 0·1493  $H_2O$ .  $C = 64·58$ ;  $H = 10·91$ .

$C_6H_{13} \cdot COOH$  requires  $C = 64·61$ ;  $H = 10·77$  per cent.

The silver salt of this acid is a white, caseous, insoluble precipitate, which, after washing well with water, alcohol, and ether, gave the following results on analysis.

0·1081 gave, on ignition, 0·0492 Ag.  $Ag = 45·51$ .

0·1622 „ „ 0·0738 Ag.  $Ag = 45·49$ .

$C_6H_{13} \cdot COOAg$  requires  $Ag = 45·57$ .

These results prove conclusively that the acid boiling at 209—210° is a heptylic acid,  $C_6H_{13} \cdot COOH$ .

As far as we have been able to find out, there have been comparatively few acids of this composition prepared, the following being a table of the known isomerides.



- (1) Normal heptylic acid,  $\text{CH}_3 \cdot [\text{CH}_2]_5 \cdot \text{COOH}$  ..... b. p.  $220.4^\circ$
- (2) Methylbutylacetic acid,  $\text{CH}_3 \cdot [\text{CH}_2]_3 \cdot \text{CH}(\text{CH}_3) \cdot \text{COOH}$  ,, 210
- (3) *iso*-Oenanthic acid, constitution unknown ..... b. p. 210—213
- (4) *iso*-Amylacetic acid,  $\text{CH}(\text{CH}_3)_2 \cdot [\text{CH}_2]_3 \cdot \text{COOH}$  ,, 208—210
- (5) Methyl-diethylacetic acid,  $\text{C}(\text{C}_2\text{H}_5)_2 \cdot [\text{CH}_3] \cdot \text{COOH}$  ,, 207—208
- (6) Ethylpropylacetic acid,  $\text{CH}_3 \cdot [\text{CH}_2]_2 \cdot \text{CH}(\text{C}_2\text{H}_5) \cdot \text{COOH}$  b. p.  $209.2^\circ$
- (7) Methylisobutylacetic acid,  $\text{CH}_3 \cdot \text{CH}(\text{C}_4\text{H}_9) \cdot \text{COOH}$  ... ,, 205
- (8) Methylisopropylpropionic acid,  
 $\text{CH}(\text{CH}_3)_2 \cdot \text{CH}(\text{CH}_3) \cdot \text{CH}_2 \cdot \text{COOH}$  (?) ..... ,, 220

It will be seen from this table that several of these acids boil at the same temperature as our hexylic acid, but as the anilides of the acids boiling between  $207$ — $213^\circ$  have not been prepared, it is impossible to decide whether or not any one of these is identical with the acid from camphoric acid.

At first we thought it probable that our acid might be isoamylacetic acid, and we therefore prepared this acid, and converted it into its anilide; this, however, melts at  $75^\circ$ , and is quite different in its solubilities and appearance from our anilide.

We are for several reasons inclined to think that our acid is a dimethylethylpropionic acid of the formula



and we propose to synthesise this acid with the view to decide this point.

#### *Examination of the Acids Boiling above $220^\circ$ .*

The portion of the acids boiling above  $220^\circ$ , weighing about 80 grams, was submitted to repeated fractionation, and ultimately the following quantities were obtained.

$220$ — $225^\circ$ = 7 grams.	$235$ — $240^\circ$ = 9 grams.
$225$ — $230$ = 14 ,,	$240$ — $245$ = 15 ,,
$230$ — $235$ = 15 ,,	$245$ — $250$ = 6 ,,

As during the distillations it was noticed that the temperature always remained constant for a considerable time at  $230$ — $232^\circ$  (750 mm.), a small quantity boiling at this temperature was converted into the anilide, in the hope that it might crystallise well, but this was not the case, and the same remark applies to the fraction  $240$ — $245^\circ$ . The fraction  $225$ — $235^\circ$  was now submitted 10 times to most careful fractionation, and ultimately 9 grams of an acid were obtained, boiling almost constantly at  $230$ — $232^\circ$  (750 mm.). On analysis, it gave the following results.

0.1074 gave 0.2602  $\text{CO}_2$  and 0.1032  $\text{H}_2\text{O}$ . C = 66.09; H = 10.68.

0.1610 ,, 0.3923  $\text{CO}_2$  ,, 0.1591  $\text{H}_2\text{O}$ . C = 66.44; H = 10.99.

$\text{C}_7\text{H}_{15} \cdot \text{COOH}$  requires C = 66.66; H = 11.11 per cent.

The slightly alkaline solution of the ammonium salt was precipitated fractionally with silver nitrate, and the three fractions of silver salt thus obtained gave the following results on analysis.

I.	0.1676	gave, on ignition,	0.0720	Ag.	Ag = 42.95.
II.	0.1483	„	„	0.0641	Ag. Ag = 43.23.
III.	0.2224	„	„	0.0965	Ag. Ag = 43.39.
$C_7H_{15} \cdot COOAg$ requires Ag = 43.03 per cent.					

This close agreement of the three fractions of the silver salt with the formula  $C_7H_{15} \cdot COOAg$  appears to indicate that the fraction 230—232° consists either of a pure acid or a mixture of isomeric acids of this formula. The former alternative seems to us to be the more probable.

*Oxidation of the Acid Boiling at 230—232°.*—In order, if possible, to obtain some clue as to the nature of this acid, the whole quantity which remained after the above analyses had been made was submitted to oxidation with potassium permanganate. As the acid is only very slowly attacked by alkaline permanganate in the cold, the solution of the acid in sodium carbonate was heated to boiling, and then small quantities of the oxidising agent added, until the oxidation appeared to become sluggish. The excess of permanganate was then destroyed by sodium hydrogen sulphite, the manganese precipitate removed by filtration, and the filtrate and washings concentrated; the liquid was then acidified with sulphuric acid and distilled with steam as long as any unchanged acid passed over. The distillate was made alkaline and oxidised as before, the operation being repeated until no unchanged acid distilled with the steam. The last steam distillate, on being neutralised with carbonate of soda and evaporated to dryness, gave a considerable quantity of a sodium salt the acid from which nearly all passed over below 150° and appeared to consist mainly of acetic and propionic acids.

The residual liquors resulting from the oxidations were concentrated, acidified with dilute sulphuric acid, saturated with ammonium sulphate, and extracted 10 times with pure ether. The ethereal solution, after drying over calcium chloride and evaporating, deposited an almost colourless oil which, on distillation under reduced pressure (40 mm.), yielded a considerable quantity of a fraction boiling at about 160—175°; as this dissolved with difficulty in sodium carbonate solution, it evidently consisted mainly of an anhydride. The whole was, therefore, dissolved in hot dilute caustic soda, a small quantity of a neutral oil removed by ether, and the acid again extracted from the solution after acidification, in the usual way. The oily acid thus obtained, when kept for some weeks in an ice chest, deposited crystals which were dried on porous porcelain, dissolved in a little water and the solution saturated with hydrogen chloride. In a short time, colourless crystals

separated which, after recrystallisation, melted at  $180^{\circ}$  and were found on analysis to consist of succinic acid.

0.1450 gave 0.2160  $\text{CO}_2$  and 0.0688  $\text{H}_2\text{O}$ .  $\text{C} = 40.63$ ;  $\text{H} = 5.27$ .

$\text{COOH} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{COOH}$  requires  $\text{C} = 40.68$ ;  $\text{H} = 5.08$  per cent.

The mother liquor from the succinic acid, when allowed to evaporate nearly to dryness over potash in a vacuum desiccator, deposited nodular crystals and some leaflets of succinic acid; the former were easily separated mechanically and after twice crystallising from hydrochloric acid were analysed.

0.1002 gave 0.1803  $\text{CO}_2$  and 0.0628  $\text{H}_2\text{O}$ .  $\text{C} = 49.10$ ;  $\text{H} = 6.97$ .

$\text{C}_8\text{H}_{10}\text{O}_4 = \text{COOH} \cdot \text{CH}(\text{CH}_3) \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{COOH}$  requires  $\text{C} = 49.32$ ;  
 $\text{H} = 6.85$  per cent.

The melting point of the crystals was  $75-77^{\circ}$ , and the general appearance and properties of the acid indicated that it was  $\alpha$ -methylglutaric acid (m. p.  $77-78^{\circ}$ ).

In order to confirm this, the remainder of the acid was converted into the anilic acid, which melted at  $112-113^{\circ}$ ; Auwers (*Annalen*, 292, 210) gives  $114-115^{\circ}$  as the melting point of methylglutaranilic acid. It seems, therefore, that the principal products of the oxidation of the acid boiling at  $230-232^{\circ}$  are succinic acid,  $\alpha$ -methylglutaric acid, and fatty acids of low boiling point. This acid does not appear to be identical with any of the known acids,  $\text{C}_8\text{H}_{16}\text{O}_2$ , and we are inclined to believe that its constitution is represented by the formula  $^*\text{CH}(\text{CH}_3)_2 \cdot \text{CH}(\text{CH}_3) \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{COOH}$ , or methylisopropylbutyric acid, in which case, if oxidation took place at the carbon atom marked \*, the formation of methylglutaric acid under these conditions could be readily understood.

It will be seen from the table given at the head of this section that a considerable quantity (15 grams) of the acids boiled at about  $240-245^{\circ}$ , and in order to examine this portion the fraction  $235-250^{\circ}$ , weighing 30 grams, was very carefully fractionated (5 times); in this way, about 9 grams of an acid were obtained boiling at  $240-242^{\circ}$ , and giving the following results on analysis.

0.1228 gave 0.3090  $\text{CO}_2$  and 0.1234  $\text{H}_2\text{O}$ .  $\text{C} = 68.69$ ;  $\text{H} = 11.16$ .

$\text{C}_8\text{H}_{17} \cdot \text{COOH}$  requires  $\text{C} = 68.35$ ;  $\text{H} = 11.39$  per cent.

On examining this acid, it was found that it contained a small quantity of an unsaturated compound, undoubtedly the acid  $\text{C}_8\text{H}_{15} \cdot \text{COOH}$  referred to in describing the acids obtained from camphoric acid by fusion with caustic soda (p. 36). In order to remove this, the whole of the fraction  $240-242^{\circ}$  was dissolved in dilute sodium carbonate,

mixed with ice, and, while well agitated with a turbine (and also by passing a rapid current of carbonic anhydride), a cold saturated solution of permanganate was run in drop by drop until the colour remained permanent. The solution was then heated to boiling, filtered, the filtrate and washings of the manganese precipitate concentrated, the residue acidified, and the oily acid extracted with ether. The ethereal solution, after drying and evaporating, deposited 7.5 grams of an oil which, on distillation, passed over completely between  $240^{\circ}$  and  $245^{\circ}$ , and nearly all at  $240$ — $242^{\circ}$ . A portion of the substance boiling at  $241^{\circ}$  was analysed.

0.1353 gave 0.3377  $\text{CO}_2$  and 0.1390  $\text{H}_2\text{O}$ .  $\text{C} = 68.07$ ;  $\text{H} = 11.41$ .

$\text{C}_8\text{H}_{17}\cdot\text{COOH}$  requires  $\text{C} = 68.35$ ;  $\text{H} = 11.39$  per cent.

The silver salt, prepared from the ammonium salt in the usual way, is a white, amorphous precipitate which was analysed after washing successively with water, methylic alcohol, and ether.

0.1350, on ignition, gave 0.0553  $\text{Ag}$ .  $\text{Ag} = 40.96$ .

$\text{C}_8\text{H}_{17}\cdot\text{COOAg}$  requires  $\text{Ag} = 40.75$  per cent.

These results clearly indicate that the acid boiling at  $240$ — $242^{\circ}$  is a fatty acid of the composition  $\text{C}_8\text{H}_{17}\cdot\text{COOH}$ , and as this acid contains only one carbon atom less than camphoric acid itself, it would be most interesting if its constitution could be elucidated. The only acids of this formula which appear to have been prepared are.

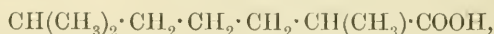
Nonylic acid (pelargonic acid),  $\text{CH}_3[\text{CH}_2]_7\cdot\text{COOH}\dots$  b. p.  $253$ — $254^{\circ}$ .

*iso*-Nonylic acid,  $\text{CH}_3\cdot[\text{CH}_2]_5\cdot\text{CH}(\text{CH}_3)\cdot\text{COOH}\dots\dots$  b. p.  $246^{\circ}$ .

Heptylacetic acid,  $\text{CH}_3\cdot[\text{CH}_2]_4\cdot\text{CH}(\text{CH}_3)\cdot\text{CH}_2\cdot\text{COOH}$  b. p.  $232^{\circ}$ .

but these are obviously not identical with our acid.

With the small amount of material at our disposal, we experimented on the action of oxidising agents on the acid, and obtained, with chromic acid, an acid which showed all the properties of  $\alpha$ -methylglutaric acid, but which we did not obtain in quantity sufficient for analysis. Unfortunately, in spite of numerous experiments, no further clue to the constitution of this acid could be obtained, and we can only suggest that its constitution may possibly be expressed by the formula



or by some formula closely allied to this.

*Isopropylsuccinic Acid (Pimelic Acid),*



It was explained on p. 11 that 856 grams of oil (A and B) was extracted from the residues obtained after the volatile acids formed

during the fusion of camphoric acid with caustic potash had been distilled off with steam. The whole of this, in quantities of 50 grams at a time, was heated with acetyl chloride (100 grams) for 2 hours in a reflux apparatus, the acetyl chloride distilled off, and the residue fractionated under a pressure of 46 mm.; it began to boil at  $150^{\circ}$ , but very little passed over below  $160^{\circ}$ , then the thermometer remained constant for a long time, about 60 per cent. of the whole passing over between  $160^{\circ}$  and  $170^{\circ}$ ; the temperature then rose rapidly, the remaining liquid distilling between  $185^{\circ}$  and  $230^{\circ}$ . The fraction  $160$ — $170^{\circ}$ , on redistillation, yielded a very large quantity of a colourless oil boiling constantly at  $164^{\circ}$  (45 mm.); this, on analysis and subsequent examination, was found to consist of pure isopropylsuccinic anhydride.

0.0974 gave 0.2105  $\text{CO}_2$  and 0.0618  $\text{H}_2\text{O}$ .  $\text{C} = 58.95$ ;  $\text{H} = 7.04$ .

$\text{C}_7\text{H}_{10}\text{O}_3$  requires  $\text{C} = 59.15$ ;  $\text{H} = 7.04$  per cent.

A portion of this anhydride was converted into the acid by dissolving it in caustic soda, acidifying, and extracting with ether, &c., when it solidified completely on cooling, and after crystallisation from benzene, melted at about  $115$ — $116^{\circ}$ .

0.1192 gave 0.2288  $\text{CO}_2$  and 0.0804  $\text{H}_2\text{O}$ .  $\text{C} = 52.34$ ;  $\text{H} = 7.49$ .

$\text{C}_7\text{H}_{12}\text{O}_4$  requires  $\text{C} = 52.50$ ;  $\text{H} = 7.50$  per cent.

Tiemann (*Ber.*, 1895, 28, 2152) states that pimelic acid (isopropylsuccinic acid) may be obtained, melting sharply at  $118^{\circ}$ , by precipitating its chloroform solution with light petroleum, but we were not able to confirm this; the melting point was never sharp, and this is accounted for by the fact that, at its melting point, pimelic acid is slowly converted into its oily anhydride. With the large quantities of pimelic acid at our disposal, we have, when using benzene as a solvent, repeatedly obtained crystals nearly an inch in length.

#### *Dihydrocamphoric Acid*, $\text{C}_{10}\text{H}_{18}\text{O}_4$ .

As mentioned in the preceding section, an oil was obtained boiling at  $185$ — $230^{\circ}$  (45 mm.); this fraction weighed about 70 grams, and its investigation has given very interesting results. The whole was boiled in a reflux apparatus with excess of caustic soda solution, when it was noticed that a small quantity of an oil, smelling strongly of peppermint, did not dissolve; this neutral oil, which may be provisionally called A, was removed by means of ether, and will be described later on in detail; in its crude state, it weighed 8 grams. The alkaline solution, when acidified with sulphuric acid, extracted with ether, &c., yielded 74 grams of a viscid oil. This was dissolved in a slight excess of ammonia, and the solution boiled with excess of a strong solution



of calcium chloride, when a large quantity of the sparingly soluble calcium pimelate was precipitated; the acid obtained from this, after purification, melted at about  $115-116^{\circ}$ , and consisted of pimelic acid as the results of the analysis show.

0.1240 gave 0.2380  $\text{CO}_2$  and 0.0849  $\text{H}_2\text{O}$ .  $\text{C} = 52.26$ ;  $\text{H} = 7.61$ .

$\text{C}_7\text{H}_{12}\text{O}_4$  requires  $\text{C} = 52.50$ ;  $\text{H} = 7.50$  per cent.

The solution of the ammonium salt thus completely freed from pimelic acid was acidified with sulphuric acid, extracted with ether, &c., when 47 grams of a nearly colourless oil was obtained, from which, however, only very small quantities of solid matter separated on standing. The whole was accordingly again dissolved in a slight excess of ammonia and the solution mixed with excess of zinc chloride, when an immediate and copious precipitate was formed; this was collected, and the filtrate heated to boiling, when a further quantity of a zinc salt separated. The free acids obtained from these zinc salts weighed 7 grams and 6 grams respectively; they were light coloured oils which solidified partially after long standing. The acid recovered in the usual way from the filtrate from the zinc salts weighed 28 grams, and when heated again in exactly the same manner with calcium chloride and zinc chloride, it yielded no calcium salt, although appreciable quantities of the zinc salts were obtained.

All the semi-solid residues of the acids obtained by decomposing the zinc salts were spread on porous porcelain until the oily mother liquor had been completely absorbed, when an almost colourless acid was obtained, which, after crystallisation from water, melted sharply at  $105^{\circ}$ .

Tiemann (*Ber.*, 1895, 28, 2153), by a similar process, obtained an acid melting at  $140^{\circ}$  from the acids formed in his experiments on the fusion of camphoric acid with caustic potash; this he found to be a mixture of ordinary *d*-camphoric acid and *d-cis*trans-camphoric acid. In our experiments, although we were unable to isolate an acid melting at  $140^{\circ}$ , it seemed possible that the acid of melting point  $105^{\circ}$  might still be a mixture of the two camphoric acids present in molecular proportions differing from those of Tiemann's substance, and in order to test this assumption, we treated the acid of melting point  $105^{\circ}$  by the method recommended by Aschan (*Ber.*, 1894, 27, 2003) for separating these isomeric camphoric acids.

The acid (5 grams) was treated in the cold with acetyl chloride (18 grams), the excess of chloride removed by aspirating dry air through the product, and the solid residue treated in the cold with dilute soda. If the original acid had been a mixture of *d*-camphoric acid and *d-cis*trans-camphoric acid, the former would have been converted into camphoric anhydride by the acetyl chloride, whereas the latter would have remained unattacked; on subsequently treating the product

with cold soda, the camphoric anhydride would have remained undissolved. Our product, however, dissolved readily and completely, and on acidifying the alkaline solution with hydrochloric acid and extracting with ether, the acid melting at  $105^{\circ}$  was recovered. It cannot, therefore, be a mixture of isomeric camphoric acids.

This is an important experiment, as the analysis of the new acid shows that it differs from camphoric acid only in containing two additional hydrogen atoms, and we therefore propose to name it *dihydrocamphoric acid*. The following were the numbers found on analysis.

0.1316 gave 0.2874  $\text{CO}_2$  and 0.1033  $\text{H}_2\text{O}$ . C = 59.56; H = 8.73.

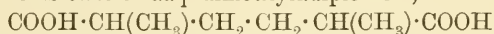
0.1184 „ 0.2574  $\text{CO}_2$  „ 0.0940  $\text{H}_2\text{O}$ . C = 59.30; H = 8.78.

0.1025 „ 0.2230  $\text{CO}_2$  „ 0.0817  $\text{H}_2\text{O}$ . C = 59.41; H = 8.84.

$\text{C}_{10}\text{H}_{18}\text{O}_4$  requires C = 59.40; H = 8.91 per cent.

This beautiful acid, when pure, melts at  $105$ — $106^{\circ}$ ; it is sparingly soluble in cold water, readily in boiling water, and usually separates on cooling as an oil which, however, rapidly solidifies. It is readily soluble in alcohol, benzene, ethylic acetate, chloroform, and hot light petroleum, also in hot dilute formic acid (sp. gr. 1.06), separating from the latter on cooling, especially if the liquid is vigorously stirred, almost completely in curious nodular masses; formic acid of this strength is undoubtedly the best solvent from which to crystallise the acid, as its separation in the form of an oil is thus avoided.

Dihydrocamphoric acid is inactive; 1.2747 grams dissolved in 55 c.c. of alcohol gave no rotation in a 2 dm. tube of a Laurent's polarimeter. The dissociation constant for the electric conductivity of dihydrocamphoric acid was found by Dr. Ewan to be  $K = 0.00415$ ; this value is about the same as that of  $\alpha\alpha_1$ -dimethyladipic acid,



( $K = 0.0042$ ), and nearly twice as large as that of camphoric acid ( $K = 0.0025$ ).

*Salts of Dihydrocamphoric Acid.*—The silver salt,  $\text{C}_8\text{H}_{16}(\text{COOAg})_2$ , which was prepared by precipitating a warm, slightly alkaline solution of the ammonium salt with silver nitrate, is an amorphous, very insoluble precipitate which, after washing with water and drying, gave the following results on analysis.

0.1132 gave 0.1210  $\text{CO}_2$ , 0.0412  $\text{H}_2\text{O}$  and 0.0583 Ag. C = 29.15; H = 4.05; Ag = 51.50.

Additional silver determinations gave Ag = 51.74, 51.63, 51.82.

$\text{C}_8\text{H}_{16}(\text{COOAg})_2$  requires C = 28.85; H = 3.85; Ag = 51.92 per cent.



*Oxidation of Dihydrocamphoric Acid.*

Dihydrocamphoric acid is only very slowly attacked by oxidising agents, and even after boiling with nitric acid for some time a considerable quantity of the acid may be recovered unchanged; potassium permanganate, moreover, is not decolorised by a cold solution of the acid in sodium carbonate even after half an hour. In order, if possible, to obtain some clue to the constitution of the acid, 2 grams were dissolved in dilute soda solution (containing 1 gram NaOH), a solution of 4 grams of permanganate added, the whole diluted to 250 c.c., and left for four weeks at the ordinary temperature, the procedure being exactly similar to that described by Balbiano (*Ber.*, 1892, **25**, 640) in his experiments on the oxidation of camphoric acid to the acid  $C_9H_{16}O_6$ .

Oxidation took place very slowly, but at the end of four weeks nearly the whole of the permanganate had been decolorised; the last traces were destroyed by sodium hydrogen sulphite, and the whole was then heated to boiling, filtered, concentrated, acidified, and extracted with ether after saturation with ammonium sulphate. The residue obtained on distilling off the ether weighed nearly 2 grams, smelt strongly of acetic acid, and, on standing, deposited crystals which were found to consist of unchanged dihydrocamphoric acid. The precipitate, extracted with ether in a Soxhlet apparatus, yielded a small quantity of a viscid oil which appeared to contain a ketonic acid, since its solution in potash gave an immediate precipitate of bromoform with bromine; unfortunately, this oil did not give a characteristic semicarbazide or hydrazone, and its nature therefore could not be ascertained.

In order, if possible, to be in a position to carry out this experiment with larger quantities of dihydrocamphoric acid, we endeavoured to prepare it by fusing camphoric acid with potash in the presence of zinc dust, but although the conditions were varied greatly, we did not succeed in obtaining even a trace of the acid in this way.

*Anhydride of Dihydrocamphoric Acid and Formation of  
Dihydrocamphoketone,  $C_9H_{16}O$ .*

When dihydrocamphoric acid is rapidly heated in small quantities in a test tube, the greater portion sublimes unchanged, but the anhydride may be readily obtained by heating the pure acid (2 grams) with pure acetic anhydride (8 grams) in a reflux apparatus for about 15 minutes, and exposing the clear solution in a vacuum desiccator over solid potash and sulphuric acid for about 14 days until the odour of acetic anhydride has entirely disappeared. The gummy residue,

which could not be made to crystallise, gave results on analysis which agree approximately with those required for dihydrocamphoric anhydride.

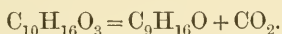
0·1530 gave 0·3629  $\text{CO}_2$  and 0·1194  $\text{H}_2\text{O}$ .  $\text{C} = 64\cdot70$ ;  $\text{H} = 8\cdot66$ .

0·1379 „ 0·3271  $\text{CO}_2$  „ 0·1073  $\text{H}_2\text{O}$ .  $\text{C} = 64\cdot61$ ;  $\text{H} = 8\cdot64$ .

$\text{C}_{10}\text{H}_{16}\text{O}_3$  requires  $\text{C} = 65\cdot22$ ;  $\text{H} = 8\cdot69$  per cent.

This anhydride is only very slowly attacked by boiling water, but it dissolves in boiling potash solution, and, on acidifying the well-cooled alkaline solution, dihydrocamphoric acid is precipitated as an oil which rapidly solidifies, and then melts at  $103\text{--}104^\circ$ .

When heated to boiling at the ordinary pressure, the anhydride undergoes a very remarkable decomposition, carbonic anhydride being eliminated, and a new ketone,  $\text{C}_9\text{H}_{16}\text{O}$ , which we have called *dihydrocamphoketone*, formed,



In order to prepare this ketone in quantity sufficient for investigation, the anhydride obtained from 5 grams of dihydrocamphoric acid was heated to boiling in a small reflux apparatus for a few minutes, until carbon dioxide ceased to be evolved, and the residue was then distilled over completely. The distillate, which had a very penetrating odour of peppermint, was warmed with dilute potash solution for some time, and the insoluble oily ketone removed by means of ether; the alkaline solution, when acidified and extracted with ether in the usual way, yielded a small quantity (0·7 gram) of dihydrocamphoric acid, which had escaped decomposition.

The ethereal solution of the ketone after being washed with water, dried, and the ether distilled off, left nearly 4 grams of a residue, which on twice fractioning distilled almost constantly at  $180\text{--}181^\circ$  and gave the following numbers on analysis.

0·1336 gave 0·3761  $\text{CO}_2$  and 0·1343  $\text{H}_2\text{O}$ .  $\text{C} = 76\cdot72$ ;  $\text{H} = 11\cdot15$ .

0·1069 „ 0·3025  $\text{CO}_2$  „ 0·1099  $\text{H}_2\text{O}$ .  $\text{C} = 77\cdot17$ ;  $\text{H} = 11\cdot42$ .

$\text{C}_9\text{H}_{16}\text{O}$  requires  $\text{C} = 77\cdot14$ ;  $\text{H} = 11\cdot43$  per cent.

Dihydrocamphoketone is a volatile liquid having a very pronounced odour of peppermint; it combines readily with phenylhydrazine, hydroxylamine, and semicarbazide, the semicarbazone being the most characteristic derivative.

*Dihydrocamphoketone semicarbazone* was prepared by mixing the pure ketone with an excess of a saturated solution of semicarbazide hydrochloride, and adding a strong solution of sodium acetate and enough alcohol to make a clear solution; the liquid was then heated at  $80^\circ$  for 15 minutes and left overnight in the ice chest, when the semi-

carbazone separated almost completely in colourless needles. These, after being drained on a porous plate, washed with water and recrystallised from alcohol, were obtained as a white, sandy powder.

0.1231 gave 0.2728  $\text{CO}_2$  and 0.1122  $\text{H}_2\text{O}$ .  $\text{C} = 60.44$ ;  $\text{H} = 10.07$ .

0.1530 „ 27.8 c.c. moist nitrogen at  $17^\circ$  and 758 mm.  $\text{N} = 21.04$ .  
 $\text{C}_8\text{H}_{16}:\text{C}:\text{N}:\text{NH}\cdot\text{CO}\cdot\text{NH}_2$  requires  $\text{C} = 60.91$ ;  $\text{H} = 9.65$ ;  $\text{N} = 21.32$  %.

The semicarbazone of dihydrocamphoketone, when moderately rapidly heated, melts at  $202\text{--}203^\circ$ , with incipient decomposition; it is almost insoluble in water and cold alcohol, and only sparingly soluble in boiling alcohol, so that it is necessary to use considerable quantities of this solvent in recrystallising it.

*Dihydrocamphoketoxime*,  $\text{C}_8\text{H}_{16}:\text{C}:\text{NOH}$ .—In order to prepare this, the pure ketone (2 grams) was dissolved in methylic alcohol, a concentrated aqueous solution of hydroxylamine hydrochloride (2.5 grams) added, and then a solution of potash (5 grams) in methylic alcohol. After two days, the methylic alcohol was removed by gently heating on the water bath, and the residue was diluted, acidified, and extracted with ether; this, after being washed and dried, left an oily residue, which, even after being kept for six days in a vacuum desiccator over sulphuric acid at  $0^\circ$ , did not show any signs of solidifying. It was analysed, with the following result.

0.1471 gave 12.5 c.c. moist nitrogen at  $16^\circ$  and 760 mm.  $\text{N} = 9.90$ .

$\text{C}_8\text{H}_{16}:\text{C}:\text{NOH}$  requires  $\text{N} = 9.03$  per cent.

Although these numbers do not agree so closely as might be desired, there can be no doubt that the substance is the oxime of dihydrocamphoketone, and many experiments were made (in the hope of being able to ascertain the constitution of the ketone) on the action of acetyl chloride and of sulphuric acid on the oxime, following Beckmann's directions, but without result. When mixed with acetyl chloride, a most violent action takes place spontaneously with formation of an intensely deep crimson sticky mass, from which nothing definite could be isolated.

It was stated on page 23 that 8 grams of a neutral pungent oil, called  $\Delta$ , were obtained when the fractions of the acids distilling between  $185$  and  $230^\circ$  (at 45 mm.) was treated with potash; on distillation, rather more than half of this passed over between  $175^\circ$  and  $195^\circ$  leaving, however, a considerable quantity of a dark brown residue of very high boiling point which was not further examined. The portion which distilled between  $175^\circ$  and  $195^\circ$ , on twice refractionating, yielded nearly 3 grams of a limpid oil boiling at  $179\text{--}181^\circ$  and smelling strongly of peppermint.

0.1611 gave 0.4538  $\text{CO}_2$  and 0.1660  $\text{H}_2\text{O}$ .  $\text{C} = 76.82$ ;  $\text{H} = 11.46$ .

0.1449 „ 0.4078  $\text{CO}_2$  „ 0.1465  $\text{H}_2\text{O}$ .  $\text{C} = 76.69$ ;  $\text{H} = 11.25$ .

$\text{C}_9\text{H}_{16}\text{O}$  requires  $\text{C} = 77.14$ ;  $\text{H} = 11.43$  per cent.

On careful examination, and especially by the preparation of the semicarbazone melting at  $202\text{--}203^\circ$ , it was soon found that this oil was dihydrocamphoketone, and its formation in the manner explained is no doubt due to the partial decomposition of some of the anhydride of dihydrocamphoric acid, which must be present in the fraction of the anhydrides boiling at about  $180\text{--}230^\circ$  (45 mm.).

### *Oxidation of Dihydrocamphoketone.*

This experiment was carried out as follows. About 50 c.c. of dilute nitric acid (sp. gr. 1.15) was heated to boiling in a flask into the neck of which a condenser had been ground, the flask was then removed from the sand-bath and 5 grams of the pure ketone added drop by drop through the condenser tube, when oxidation took place so vigorously that the liquid was kept boiling without external application of heat. When all the ketone had been added, the mixture was kept boiling for about half an hour, and then evaporated on a water bath, the residue being treated repeatedly with water to ensure the removal of all but the last traces of the nitric acid. Finally, the residue, which on standing overnight had deposited crystals, was dissolved in water, made slightly alkaline with ammonia, and boiled with an excess of calcium chloride solution. The filtrate from the precipitate of calcium oxalate thus formed was acidified, and the solution, after being saturated with ammonium sulphate, was extracted 25 times with pure ether. The ethereal solution, dried by calcium chloride and evaporated to a small bulk, was left for some days in a closed vessel at  $0^\circ$ , when crystals of succinic acid melting at  $183^\circ$  separated.

0.1278 gave 0.1914  $\text{CO}_2$  and 0.0590  $\text{H}_2\text{O}$ .  $\text{C} = 40.82$ ;  $\text{H} = 5.12$ .

$\text{COOH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{COOH}$  requires  $\text{C} = 40.68$ ;  $\text{H} = 5.10$  per cent.

The ethereal filtrate from the succinic acid was evaporated to dryness and the syrupy residue (2.6 grams), which did not crystallise even on long standing, was heated with excess of acetic anhydride for 1 hour. The acetic anhydride was then very slowly distilled off and the residue fractionated under reduced pressure, when nearly 2 grams passed over at  $160\text{--}170^\circ$  (35 mm.) as a moderately thick oil, which was insoluble in water, but dissolved slowly in hot potash solution: that is, it had the properties of an anhydride. The whole was now dissolved in a little pure benzene, the solution mixed with aniline (2 grams), and kept at  $0^\circ$  for 7 days in a closed vessel. The crystals

which had separated, after being left in contact with porous porcelain until quite colourless, were crystallised from dilute alcohol, by which means a substance melting at  $159^{\circ}$  was obtained.

0.0720 gave 3.5 c.c. moist nitrogen at  $17^{\circ}$  and 754 mm.  $N = 5.60$ .

$\text{COOH} \cdot \text{C}_6\text{H}_{12} \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_6\text{H}_5$  requires  $N = 5.62$  per cent.

This anilic acid was heated for 1 hour in a sealed tube at  $140^{\circ}$  with 5 c.c. of a solution of hydrogen chloride in glacial acetic acid, and the product, after being allowed to evaporate to dryness over potash in a vacuum desiccator, was dissolved in a little water, saturated with ammonium sulphate, and extracted with ether in the usual way. The oil thus obtained rapidly and completely solidified, and on dissolving it in a few drops of water, saturating with hydrogen chloride, and allowing it to stand, it deposited colourless crystals; these were drained on porous porcelain and dried over potash in a desiccator, when they melted at  $94^{\circ}$ .

0.0875 gave 0.1760  $\text{CO}_2$  and 0.0661  $\text{H}_2\text{O}$ .  $C = 54.85$ ;  $H = 8.39$ .

$\text{C}_8\text{H}_{14}\text{O}_4$  requires  $C = 55.18$ ;  $H = 8.04$  per cent.

The properties of this acid point to its being identical with the trimethylglutaric acid,  $\text{COOH} \cdot \text{CH}(\text{CH}_3) \cdot \text{C}(\text{CH}_3)_2 \cdot \text{CH}_2 \cdot \text{COOH}$ , which Balbiano (*Ber.*, 1895, 28, 1507) obtained from camphoric acid, as this acid melts at  $94$ – $95^{\circ}$  and gives an anilic acid melting at  $158$ – $159^{\circ}$ . Unfortunately, the quantity of our pure acid was not sufficient to allow of its being converted into the anhydride, as the melting point of this would have conclusively settled the question of the identity of the two acids.

#### FUSION OF CAMPHORIC ACID WITH CAUSTIC SODA.

In these experiments, 4 kilos. of camphoric acid were fused in quantities of 500 grams, with about eight times its weight of caustic soda, in a precisely similar manner and in the same apparatus as was used in the potash experiments. The slight differences in behaviour observed during the operation were the following.

1st. The action was apparently much more vigorous, and great care had to be taken in order to prevent the melt from frothing over.

2nd. The odour of menthol mentioned in the case of the caustic potash fusions was much more pronounced in this case.

3rd. The colour of the cold melt was pale brown.

4th. The whole operation lasted a somewhat shorter time, namely, from  $2\frac{1}{2}$ –3 hours, instead of from  $3$ – $3\frac{1}{2}$ , as in the case of the fusion with potash.

*Working up of the Product.*—The process was carried out exactly as



described in the case of the potash melts (p. 11). The following numbers are of importance, as showing roughly the difference in behaviour of camphoric acid when fused with soda as compared with its behaviour with potash.

The weight of the sodium salts obtained by neutralisation and subsequent evaporation of the distillate from the steam distillation was  $1\frac{1}{2}$  kilos. (potash melts 4 kilos.), and the weight of free fatty acids obtained from the salts was 715 grams (potash melts 2·3 kilos.).

*Volatile Acids formed during the Fusion of Camphoric Acid with Soda.*

After a first rough fractionation giving the following numbers,

Fraction.	Weight in grams.
50—100°	71
100—125	13
125—135	10
135—150	207
above 150	360

the acids were dried over anhydrous sodium sulphate and frequently distilled, the process of drying being repeated after each distillation. The final numbers obtained were

Fraction.	Weight in grams.
50—100°	7
100—125	20
125—135	13
135—150	147
above 150	383

A few drops of the fraction 100—125°, when warmed with concentrated sulphuric acid, gave off a gas which burnt in air, and was probably carbon monoxide, produced by the decomposition of formic acid; but the amount was small.

The acids boiling above 150° yielded the following fractions.

Fraction.	Weight in grams.	Fraction.	Weight in grams.
below 150°	1	200—210°	33
150—160	1	210—220	42
160—170	16	220—230	46
170—180	38	230—240	71
180—190	51	above 240	52
190—200	35		

From the higher fractions, a small amount of solid matter separated which, from a determination of its melting point, was proved to be

pimelic (*iso*-propylsuccinic) acid. In order to remove this substance, the whole of the acids boiling above  $150^{\circ}$  were dissolved in ammonia, and subjected to steam distillation exactly in the same way as described in the purification of the acids from the potash melts (p. 13).

The accompanying table gives the results obtained after this treatment.

Fraction.	Weight in grams of acids before separation process was applied.	Weight in grams of acids after separation process was applied.	Weight in grams of oil got from the residual ammonium salts after steam distillation.
150—160°	1	5	} 20
160—170	16	18	
170—180	33	28	
180—190	51	16	
190—200	35	29	} 10
200—210	33	28	
210—220	42	21	} 22
220—230	46	30	
230—240	71	68	} 11
above 240	52	13	

The difference in the weights of the fractions of the fatty acids obtained from the potash and soda melts respectively is so marked that, for the sake of comparison, the following data are here inserted, the numbers given being the weights obtained after the distillation of the ammonium salts in steam. For this purpose, the weights have been put in percentages, calculated on the camphoric acid used, this being necessary owing to the fact that less camphoric acid was used in the soda than in the potash fusions; the most noticeable differences in the acids from the two melts are,

1st. The large amounts of the lower fractions in the potash melts as compared with the very small amounts of these fractions in the soda melts.

2nd. The comparatively large amount of the higher fractions, and in particular of the fraction 230—240°, in the “caustic soda” acids (see table, p. 33).

*Residue from the Steam Distillation.*—These residues were worked up as already described in the case of the potash melts (see p. 11). When the “crystalline residue from partial evaporation” was dissolved in acid, a thick, black scum (A) formed on the surface, which was separated by filtration; it weighed 185 grams. On extracting the filtrate with ether, 167 grams of a nearly colourless oil (B) was obtained.



Fraction.	<i>Caustic Potash.</i>	<i>Caustic Soda.</i>
	Percentage weight in grams after separation by means of ammonia.	Percentage weight in grams after separation by means of ammonia.
50—100°	0.00	0.17
100—125	14.02	0.50
125—135	6.60	0.30
135—150	5.70	3.70
150—160	0.62	0.10
160—170	0.50	0.40
170—180	0.50	0.70
180—190	0.70	0.40
190—200	0.40	0.70
200—210	0.86	0.70
210—220	0.60	0.50
220—230	1.08	0.70
230—240	0.40	1.70
above 240	0.12	0.30

The "residue from complete evaporation" gave 348 grams of a colourless oil (C).

*Volatile Acids Formed in the Fusion of Camphoric Acid with Soda.*

*The Fraction 100—125° contains Acetic Acid, CH<sub>3</sub>·COOH.*—The fractions 100—125° and 125—135° were dried in contact with concentrated sulphuric acid and refractionated in order to see whether any acetic acid could be obtained. After repeated distillation, during which most of the already small fractions passed over either below 100° or above 135°, 2.5 grams boiling between 116—120° were collected. On converting this liquid into the anilide, the product was proved to be acetanilide from its melting point and crystalline appearance.

*The Fraction 135—150° contains Propionic Acid, CH<sub>3</sub>·CH<sub>2</sub>·COOH.*—After repeated very careful fractionation with a column, an acid was isolated which distilled constantly at 140°, and was evidently propionic acid.

0.1530 gave 0.2731 CO<sub>2</sub> and 0.1156 H<sub>2</sub>O. C = 48.62; H = 8.36.

C<sub>3</sub>H<sub>6</sub>O<sub>2</sub> requires C = 48.64; H = 8.10 per cent.

The anilide of this acid was prepared by heating it with aniline and recrystallising the product from light petroleum (b. p. 100—120°); the white plates thus obtained were almost insoluble in water, more soluble in light petroleum, and very soluble in alcohol and ether. The substance melted at 103—104°.

0.2072 gave 16.8 c.c. moist nitrogen at  $15^{\circ}$  and 768 mm.  $N = 9.59$ .

$C_9H_{11}NO$  requires  $N = 9.39$  per cent.

The melting point of propionanilide as given by Sestini (*Zeitschrift für Chemie*, 1871, 35) is  $92^{\circ}$ , and by Kelbe (*Ber.*, 1883, 16, 1200) as  $105^{\circ}$ . A specimen of the anilide which we prepared from pure propionic acid and pure aniline melted at  $103$ — $104^{\circ}$ , and was identical with the anilide obtained by us as described above.

The Fraction 150— $160^{\circ}$  contains Isobutyric Acid,  $CH(CH_3)_2 \cdot COOH$ . After repeated fractionation of all the acids boiling between  $150$ — $180^{\circ}$ , it was found that the greater portion passed over between  $150^{\circ}$  and  $160^{\circ}$  (30 grams). Of this amount, all boiling between  $153$ — $157^{\circ}$  was collected separately, and a portion boiling at  $155^{\circ}$  submitted to analysis, when numbers were obtained which indicated that the acid was *iso*-butyric acid, a result confirmed by the examination of its properties.

0.1112 gave 0.2210  $CO_2$  and 0.0914  $H_2O$ .  $C = 54.22$ ;  $H = 9.12$ .

$C_4H_8O_2$  requires  $C = 54.54$ ;  $H = 9.09$  per cent.

The anilide, prepared from this acid in the usual way, crystallised from light petroleum (b. p.  $60$ — $90^{\circ}$ ) in glistening, white needles, melting at  $105^{\circ}$ .

0.1058 gave 8 c.c. moist nitrogen at  $12^{\circ}$  and 754 mm.  $N = 8.90$ .

$C_{10}H_{13}NO$  requires  $N = 8.59$  per cent.

This anilide is insoluble in cold water, but melts under boiling water to an oil which crystallises on cooling. It is insoluble in cold light petroleum (b. p.  $60$ — $90^{\circ}$ ), but dissolves readily in chloroform, alcohol, ether and boiling light petroleum.

Norton (*Amer. Chem. J.*, 7, 117) describes the anilide of isobutyric acid as a substance easily soluble in hot water and melting at  $102.5^{\circ}$ . As the melting point and solubility in water of the anilide of the acid boiling at  $153$ — $157^{\circ}$  did not agree with Norton's observations, some pure isobutyranilide was made from pure isobutyric acid. It crystallised from light petroleum (b. p.  $60$ — $90^{\circ}$ ) in colourless, feathery needles which melted at  $105^{\circ}$ ; it was almost insoluble in boiling water, but melted to a colourless oil which solidified on cooling, and agreed in every respect with the properties of the anilide obtained from the acid boiling at  $153$ — $157^{\circ}$ .

The calcium salt of this acid was prepared by boiling the purified acid with water and excess of calcium carbonate; on concentrating, the filtrate deposited colourless, glistening, feathery needles, which were collected, dried by exposure to air, and the water of crystallisation determined.

0.2012 lost 0.0518  $\text{H}_2\text{O}$  at  $155^\circ$ .  $\text{H}_2\text{O} = 25.74$ .

$(\text{C}_4\text{H}_7\text{O}_2)_2\text{Ca}, 4\text{H}_2\text{O}$  requires  $\text{H}_2\text{O} = 25.17$  per cent.

$(\text{C}_4\text{H}_7\text{O}_2)_2\text{Ca}, 5\text{H}_2\text{O}$  requires  $\text{H}_2\text{O} = 29.60$  per cent.

This number is practically identical with the one obtained for calcium isobutyrate from the potash fusions (p. 15). A calcium determination in the dry salt was made.

0.1506 gave 0.0976  $\text{CaSO}_4$ .  $\text{Ca} = 19.05$ .

$(\text{C}_4\text{H}_7\text{O}_2)_2\text{Ca}$  requires  $\text{Ca} = 18.69$  per cent.

It was pointed out in discussing the acids from the potash melts (p. 15) that the fraction  $150\text{--}170^\circ$  could, at the most, only contain traces of normal butyric acid: and it is interesting that, in the case of the acids from the soda melts, the same point is brought out, as, although *iso*-butyric acid was present in quantity, no butyric acid could be detected.

*The Investigation of the Acids from the Soda Melts boiling between  $200^\circ$  and  $250^\circ$ .*

This portion of the acids, which weighed about 160 grams, was ten times carefully fractionated, when the following fractions were obtained.

195—200° = 9 grams.	225—230° = 9 grams.
200—205 = 7 „	230—235 = 15 „
205—210 = 14 „	235—240 = 17 „
210—215 = 15 „	240—245 = 16 „
215—220 = 8 „	245—250 = 10 „
220—225 = 14 „	Residue = 4 „

The acids boiling between  $205^\circ$  and  $215^\circ$  were treated exactly in the same way as described in the case of the acids from the potash melts boiling at  $200\text{--}220^\circ$  (p. 18), and an anilide was obtained which melted at  $105^\circ$  and was sparingly soluble in light petroleum; on analysis, it gave the following results.

0.1140 gave 6.6 c.c. moist nitrogen at  $13^\circ$  and 770 mm.  $\text{N} = 6.93$ .

$\text{C}_6\text{H}_{13}\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_5$  requires  $\text{N} = 6.83$  per cent.

The anilide (8 grams) was decomposed by heating with hydrochloric acid, and the liberated fatty acid fractionated, when nearly the whole passed over at  $209\text{--}210^\circ$ , and, on analysis, gave the following result.

0.1351 gave 0.3194  $\text{CO}_2$  and 0.1304  $\text{H}_2\text{O}$ .  $\text{C} = 64.52$ ;  $\text{H} = 10.73$ .

$\text{C}_6\text{H}_{13}\cdot\text{COOH}$  requires  $\text{C} = 64.62$ .  $\text{H} = 10.77$  per cent.

The *silver salt*, prepared as usual, was analysed.

0.1197, on ignition, gave 0.0542 Ag.  $\text{Ag} = 45.28$ .

$\text{C}_6\text{H}_{13}\cdot\text{COOAg}$  requires  $\text{Ag} = 45.57$  per cent.

It is therefore clear that this acid, boiling at  $209\text{--}210^\circ$ , has the composition  $\text{C}_6\text{H}_{13}\cdot\text{COOH}$ , and as the boiling point of the acid, and the melting point and general proportion of its anilide, correspond exactly with those of the corresponding acid and anilide derived from the potash melts, there can scarcely be a doubt that the two acids are identical.

An examination of the table given at the head of this section would seem to indicate that a fatty acid boiling at  $225^\circ$  was present, but after repeated fractionation, the boiling point gradually rose, until ultimately the principal fraction came over at  $228\text{--}230^\circ$ . A small quantity boiling at  $229\text{--}230^\circ$ , collected for analysis, gave the following numbers.

0.1340 gave 0.3272  $\text{CO}_2$  and 0.1336  $\text{H}_2\text{O}$ .  $\text{C} = 66.59$ ;  $\text{H} = 11.08$ .

$\text{C}_7\text{H}_{15}\cdot\text{COOH}$  requires  $\text{C} = 66.66$ ;  $\text{H} = 11.11$  per cent.

It is very probable that this acid is the same as the acid boiling at  $230\text{--}232^\circ$  from the potash melts, but owing to the absence of characteristic derivatives, there appears to be little chance of determining either this point or the constitution of the acid.

Much more satisfactory results were obtained in examining the fraction of the acids boiling between  $235^\circ$  and  $250^\circ$ , and from this, on repeated fractionation, a considerable quantity of an acid was isolated, which boiled remarkably constantly at  $240\text{--}242^\circ$  and, on analysis, gave the following results.

0.1362 gave 0.3450  $\text{CO}_2$  and 0.1260  $\text{H}_2\text{O}$ .  $\text{C} = 69.01$ ;  $\text{H} = 10.28$ .

0.1100 „ 0.2775  $\text{CO}_2$  „ 0.1040  $\text{H}_2\text{O}$ .  $\text{C} = 68.73$ ;  $\text{H} = 10.50$ .

0.1232 „ 0.3104  $\text{CO}_2$  „ 0.1164  $\text{H}_2\text{O}$ .  $\text{C} = 68.71$ ;  $\text{H} = 10.49$ .

$\text{C}_9\text{H}_{16}\text{O}_2 = \text{C}_8\text{H}_{15}\cdot\text{COOH}$  requires  $\text{C} = 69.23$ ;  $\text{H} = 10.25$  per cent.

$\text{C}_9\text{H}_{18}\text{O}_2 = \text{C}_8\text{H}_{17}\cdot\text{COOH}$  requires  $\text{C} = 68.35$ ;  $\text{H} = 11.38$  per cent.

The *silver salt*, prepared in the usual way, and well washed with water, methylic alcohol, and ether was analysed.

0.2107 gave, on ignition, 0.0860 Ag.  $\text{Ag} = 40.81$

$\text{C}_8\text{H}_{15}\cdot\text{COOAg}$  requires  $\text{Ag} = 41.06$  per cent.

These analyses (those of the acid in particular) clearly show that the acid obtained from the soda melts and boiling at  $240\text{--}242^\circ$  is an unsaturated acid of the formula  $\text{C}_8\text{H}_{15}\cdot\text{COOH}$ ; in the case of the potash melts, however, the acid of this boiling point, although con-

taining traces of an unsaturated acid, has the formula  $C_8H_{17}\cdot COOH$ , and is a saturated acid. It will, however, be shown below that traces of the saturated acid,  $C_8H_{17}\cdot COOH$ , are present in the unsaturated acid from the soda melts, and this saturated acid is no doubt identical with that obtained from the potash melts.

The solution of the acid  $C_8H_{15}\cdot COOH$  in dilute soda reduces permanganate instantly in the cold, and also slowly decolorises a solution of bromine in chloroform. An attempt was made to prepare the dibromo-additive product of the acid, by exposing a weighed quantity to the action of dry bromine vapour in the dark, and then removing the excess of bromine by allowing the product to remain for some days over potash in a vacuum desiccator. It was found that 0.5017 gram of the oil had absorbed 0.6179 gram of bromine, corresponding with an increase in weight of 121 per cent., whereas on the assumption that a dibromo-acid of the formula  $C_8H_{15}Br_2\cdot COOH$  had been formed in this process, the increase in weight should have been 115 per cent. An analysis of the crude product gave the following result.

0.2300 gave 0.2954 AgBr.  $Br = 54.34$ .

$C_8H_{15}Br_2\cdot COOH$  requires  $Br = 50.63$  per cent.

These somewhat high results are explained by the fact that, during the bromination, besides addition, a certain amount of substitution takes place, as was shown by the formation of some hydrogen bromide during the experiment; nevertheless, the results are interesting as confirming the unsaturated nature of the above acid.

*Oxidation of the Acid  $C_8H_{15}\cdot COOH$ .*—In order to obtain, if possible, some idea of the constitution of this acid, its behaviour towards oxidising agents was investigated, and a method was adopted which had been found to give valuable results in a somewhat analogous case, namely, the oxidation of the acid, first with alkaline potassium permanganate, and then with potassium dichromate and sulphuric acid.

Eleven grams of the acid boiling at  $239-243^\circ$  were dissolved in dilute sodium carbonate, the solution mixed with a large quantity of powdered ice in a circular porcelain pan, and the whole stirred with a turbine until the temperature had sunk to  $0^\circ$ . A rapid current of carbonic anhydride was now passed in, and then a cold saturated solution of permanganate run in drop by drop until the colour just remained permanent. The product was heated to boiling, and after filtering from the manganese precipitate, both filtrate and washings were evaporated to a small bulk. The concentrated solution was then heated to  $70^\circ$  in a large flask on a water bath, and a solution of potassium dichromate in dilute sulphuric acid run in in small quantities



at a time,\* until no further action seemed to take place; the whole was then saturated with ammonium sulphate and extracted 20 times with ether.

The ethereal solution on evaporation deposited a viscid, uninviting greenish oil, which did not solidify even on long standing; ultimately, however, a crystalline acid was isolated from it in the following way. The crude product, mixed with water, in which it only partially dissolved, was submitted to distillation with steam until oily drops ceased to come over; the residue in the distilling flask was then boiled with soda to precipitate any chromium present, filtered, the filtrate evaporated, acidified and again extracted with ether. The ethereal solution, after drying and evaporating, deposited a thick oil which, after being kept for some weeks at 0°, deposited about 1 gram of a solid acid, in the form of curious nodular masses. These crystals, after being freed from the oily mother liquor, by spreading the semi-solid mass on porous porcelain, were purified by recrystallisation from hydrochloric acid, when a perfectly colourless, crystalline acid melting at 75° was obtained.

0.1200 gave 0.2152 CO<sub>2</sub> and 0.0757 H<sub>2</sub>O. C = 48.86; H = 7.00.

C<sub>6</sub>H<sub>10</sub>O<sub>4</sub> = COOH·CH(CH<sub>3</sub>)·CH<sub>2</sub>·CH<sub>2</sub>·COOH requires C = 49.32;  
H = 6.85 per cent.

The remainder of the acid was converted into the anhydride by heating with acetyl chloride, and from this the anilic acid was prepared in the usual way, and recrystallised from dilute methylic alcohol. The glistening, crystalline mass thus obtained melted at 113—115°, and showed all the properties of methylglutaric acid.

0.1238 gave 6.5 c.c. moist nitrogen at 14° and 765 mm. N = 6.20.

C<sub>12</sub>H<sub>15</sub>NO<sub>3</sub> requires N = 6.33 per cent.

From these results, it appears that the unsaturated acid, C<sub>8</sub>H<sub>15</sub>·COOH, when oxidised in the manner described above, yields *α*-methylglutaric acid as one of its decomposition products.

The oily acid which had been separated from the methylglutaric acid by distillation with steam, as explained above, was extracted with ether and carefully fractionated, when nearly half a gram passed over at 238—244°, very little product of a high or low boiling point being present.

The fraction which did not reduce permanganate in the cold was analysed.

0.1508 gave 0.3754 CO<sub>2</sub> and 0.1560 H<sub>2</sub>O. C = 67.87; H = 11.47.

C<sub>8</sub>H<sub>17</sub>·COOH requires C = 68.35; H = 11.39 per cent.

\* During the early stages of this oxidation, the odour of acetone was distinctly noticeable.



There can be no doubt that this acid is identical with the acid,  $C_8H_{17}\cdot COOH$ , obtained from the potash melts and boiling at  $240-242^\circ$ , and this experiment shows that the unsaturated acid,  $C_8H_{15}\cdot COOH$ , from the soda melts contains traces of this saturated acid.

*Acids obtained from the Residues of the Steam Distillation. Pseudo-camphoric Acid,  $C_{10}H_{16}O_4$ .*

The first treatment of the residues of the steam distillation from the soda melts was described on page 33, and in subsequently working up the various products then obtained, the black scum A, weighing 185 grams, was first investigated. This uninviting looking mass was dissolved in ether, the ethereal solution washed with very dilute hydrochloric acid, dried over calcium chloride, and the ether distilled off; the residue, in quantities of 50 grams, was then heated with acetyl chloride (100 grams) for half an hour, the excess of the latter distilled off, and the oils thus obtained submitted to fractionation under a pressure of 46 mm., when nearly the whole passed over between  $200^\circ$  and  $210^\circ$ . This oily distillate, on being well shaken for some time with excess of a dilute solution of caustic soda, left a considerable portion undissolved; this was extracted with ether, and the ethereal solution dried and evaporated, when it deposited crystals of camphoric anhydride, which after recrystallisation from alcohol melted at  $218^\circ$ .

0.1022 gave 0.2468  $CO_2$  and 0.0718  $H_2O$ .  $C = 65.87$ ;  $H = 7.80$ .

$C_{10}H_{14}O_3$  requires  $C = 65.93$ ;  $H = 7.69$  per cent.

On dissolving the anhydride in hot potash solution and acidifying, ordinary *d*-camphoric acid was deposited; it melted at  $183-184^\circ$ , and, in alcoholic solution, had a rotatory power  $[\alpha]_D = +41^\circ$ .

The alkaline solution from which the camphoric anhydride had been removed by treatment with ether, was acidified with hydrochloric acid and extracted with ether, &c.; the oily product thus obtained deposited crystals which, after being purified by spreading them on porous porcelain and repeated recrystallisation from water, melted constantly at  $119-120^\circ$ , and gave the following results on analysis.

0.1208 gave 0.2648  $CO_2$  and 0.0890  $H_2O$ .  $C = 59.77$ ;  $H = 8.19$ .

0.1186 „ 0.2602  $CO_2$  „ 0.0844  $H_2O$ .  $C = 59.84$ ;  $H = 7.93$ .

0.1580 „ 0.3486  $CO_2$  „ 0.1149  $H_2O$ .  $C = 60.17$ ;  $H = 8.08$ .

$C_{10}H_{16}O_4$  requires  $C = 60.00$ ;  $H = 8.00$  per cent.

This very interesting acid is therefore isomeric with camphoric

acid, and for this reason we have called it *pseudocamphoric acid*. Pseudocamphoric acid is readily soluble in hot water, crystallising out, on cooling, in colourless, six-sided plates with bevelled edges, usually in stellate groups; it is also readily soluble in ether, alcohol, and benzene, but only sparingly in light petroleum. The solution of the acid in dilute sodium carbonate does not decolorise permanganate in the cold, and even on boiling oxidation takes place but very slowly.

*Salts of Pseudocamphoric Acid.*—The silver salt,  $C_8H_{14}(COOAg)_2$ , is obtained as a sparingly soluble, white precipitate on adding silver nitrate to a warm, slightly alkaline solution of the ammonium salt; after being well washed and dried at  $100^\circ$ , it was analysed.

0.2106 gave 0.2230  $CO_2$ , 0.0650  $H_2O$ , and 0.1094 Ag.

C = 28.91; H = 3.42; Ag = 51.94.

Additional silver determinations gave Ag = 51.76 and 51.86.

$C_8H_{14}(COOAg)_2$  requires C = 28.98; H = 3.38; Ag = 52.17 per cent.

The neutral solution of the ammonium salt of pseudocamphoric acid shows the following behaviour with reagents.

*Barium nitrate*, no precipitate.

*Copper sulphate*, a heavy, pale blue precipitate.

*Calcium chloride*, no precipitate in the cold, but on boiling, if the solution is moderately strong, the calcium salt separates as a white, crystalline precipitate.

*Lead acetate*, a heavy, white, very insoluble precipitate.

It was noticed during these experiments that, on evaporating a neutral solution of the ammonium salt in the water bath, it becomes strongly acid.

*Pseudocamphoric Anhydride*,  $C_8H_{14}\begin{smallmatrix} \diagup CO \diagdown \\ \diagdown CO \diagup \end{smallmatrix}O$ .—In order to determine whether pseudocamphoric acid, like camphoric acid, was capable of forming an anhydride, the pure acid (2 grams) was heated with acetyl chloride (10 grams) in a reflux apparatus for 15 minutes, and the solution then allowed to remain over solid potash in a vacuum desiccator until the excess of acetyl chloride had been removed. The slightly yellowish residue, which quickly solidified, was left in contact with porous porcelain until colourless; it melted at  $52-53^\circ$  and, after recrystallisation from light petroleum, at  $53-54^\circ$ .

0.1524 gave 0.3664  $CO_2$  and 0.1066  $H_2O$ . C = 65.57; H = 7.77.

$C_{10}H_{14}O_3$  requires C = 65.93; H = 7.69 per cent.

Pseudocamphoric anhydride is readily soluble in the usual organic solvents, with the exception of light petroleum, in which it dissolves but sparingly. It distils without decomposition, and the distillate on

cooling at once solidifies to a colourless, crystalline mass melting at 52—53°.

*Pseudocamphoranilic Acid*,  $\text{COOH} \cdot \text{C}_8\text{H}_{14} \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_6\text{H}_5$ .—When the solution of pseudocamphoric anhydride in benzene was mixed with aniline, the mixture became warm and after a time deposited a few crystals. As the quantity of these, however, was but small, the whole was heated in a basin on the water bath until free from benzene, and the residue mixed with ether and allowed to stand; the white, sparingly soluble substance which separated was collected, washed with ether, and purified by recrystallisation from dilute alcohol. The colourless, glistening, crystalline mass obtained in this way consisted of pure pseudocamphoranilic acid, as the following analysis shows.

0.2218 gave 10.3 c.c. nitrogen at 20° and 731 mm.  $N = 5.15$ .

$\text{C}_{16}\text{H}_{21}\text{NO}_3$  requires  $N = 5.09$  per cent.

When heated moderately rapidly in a capillary tube, pseudocamphoranilic acid melts at 208° without decomposition; it is almost insoluble in water, benzene, and light petroleum, but readily soluble in hot alcohol and acetone. When heated in a test tube, it decomposes at a high temperature, with elimination of water, the residue distilling as a colourless oil which solidifies on rubbing. Unfortunately, the amount of material at our disposal was too small to allow of the purification of this crude substance, which is doubtless the anil of pseudocamphoric acid.

#### *Action of Sulphuric Acid on Pseudocamphoric Acid.*

As camphoric acid when heated with sulphuric acid is converted into sulphocamphylic acid with evolution of carbon monoxide,  $\text{C}_{10}\text{H}_{16}\text{O}_4 + \text{H}_2\text{SO}_4 = \text{C}_9\text{H}_{14}\text{SO}_5 + \text{CO} + 2\text{H}_2\text{O}$ , it seemed interesting to determine whether pseudocamphoric acid, under similar conditions, would undergo an analogous decomposition.

In order to investigate this point, pure pseudocamphoric acid (0.5 gram) was mixed with concentrated sulphuric acid (3 c.c.) and the mixture heated at 100° in a test tube. The crystals soon dissolved and the solution, which at first was nearly colourless, rapidly became red and finally black; there was considerable effervescence, due to the evolution of carbon dioxide, and some sulphur dioxide, but no trace of carbon monoxide could be detected. As at the end of 10 minutes the effervescence had ceased, the whole was poured into ice-cold water, when it gave a brown solution in which a light brown, flocculent precipitate was suspended. This precipitate was collected,

but its nature could not be determined, as, although a sparingly soluble, colourless, crystalline substance resembling paraxylic acid was obtained from it, the amount was too small for analysis or further investigation. The filtrate from the brown precipitate was extracted several times with ether, and the ethereal solution, after washing and drying over calcium chloride, deposited, on evaporation, a slightly brownish oil, which dissolved readily in sodium carbonate; it could not, however, be obtained in a crystalline condition, and, therefore, was not analysed: it did not contain any sulphur. This experiment shows conclusively that pseudocamphoric acid, when treated with sulphuric acid, does not yield a sulphonic acid, and therefore behaves differently from camphoric acid.

*Oxidation of Pseudocamphoric Acid.*

This experiment need not be described in detail, as it was carried out under exactly the same conditions as the oxidation of dihydrocamphoric acid (p. 26), the quantities used being pseudocamphoric acid, 1·8 grams; caustic soda, 1 gram; and potassium permanganate, 4 grams; oxidation was nearly complete after 5 weeks at the ordinary temperature. The exchanged pseudocamphoric acid (0·6 gram) was isolated, and also 1·3 grams of a thick, yellow oil, which from its behaviour with bromine and potash and with phenylhydrazine evidently contained a ketonic acid, but as no crystalline derivative could be obtained its investigation was abandoned.

Returning to the investigations of the oils obtained from the residues of the steam distillation of the soda melts (p. 33), the two products B and C were mixed and treated with acetyl chloride, exactly as described in the case of the similar acids from the potash melts (p. 23). After distilling off the excess of acetyl chloride and fractionating under reduced pressure, the following fractions were collected.

150—175°	= 150 grams
175—200	} = 390 grams
200—240	

These fractions were treated separately with excess of dilute soda, the portion remaining insoluble being extracted with ether. The combined ethereal solutions, on evaporation, deposited an oil which solidified almost completely after a time; the crystals of *d*-camphoric anhydride thus obtained, after crystallisation, melted at 218—219°.

0·1140 gave 0·2745 CO<sub>2</sub> and 0·0769 H<sub>2</sub>O. C = 65·68; H = 7·50.

C<sub>10</sub>H<sub>14</sub>O<sub>3</sub> requires C = 65·93; H = 7·69 per cent.

The three alkaline extracts were also mixed, acidified with hydrochloric acid and extracted several times with ether; the residue left on evaporating the ethereal solution was dissolved in a slight excess of ammonia and boiled with calcium chloride, when a heavy, white precipitate of calcium pimelate (isopropylsuccinate) was formed. This, when decomposed by hydrochloric acid, gave large quantities of pimelic acid which, after recrystallisation from benzene, melted at 115—116°.

0.1008 gave 0.1940 CO<sub>2</sub> and 0.0678 H<sub>2</sub>O. C=52.47; H=7.48.

C<sub>7</sub>H<sub>12</sub>O<sub>4</sub> requires C=52.50; H=7.50 per cent.

The filtrate from the calcium pimelate was treated, in the first instance, with zinc chloride exactly as described in the case of the potash melts (p. 24), but as the results were unsatisfactory, the following treatment was adopted. The concentrated solution of the ammonium salts, after acidifying, was extracted with ether in the usual way, and the thick oily product distilled under a pressure of 44 mm., collecting the fractions

165—210°; 210—235°; 235—260°.

The first of these, on standing, deposited crystals which, after crystallisation from water, melted at 117—119°, and were on analysis found to consist of pseudocamphoric acid.

On repeated fractionation, the combined fraction 210—260° yielded a considerable quantity of a very thick oil, which boiled remarkably constantly at 255—56° (50 mm.), and on analysis gave the following results.

0.1313 gave 0.2700 CO<sub>2</sub> and 0.0951 H<sub>2</sub>O. C=56.09; H=8.04.

0.1293 gave 0.2645 CO<sub>2</sub> and 0.0960 H<sub>2</sub>O. C=55.83; H=8.25 per cent.

We were for a long time very much puzzled as to the nature of this acid, and it was only after numerous experiments, extending over a long period, that we were able to determine its composition.

In the first place, we found that the oil analysed, although boiling so constantly at 254—257° (50 mm.), was nevertheless not quite pure, as, when mixed with water, in which the bulk of the substance is excessively soluble, a small quantity remained undissolved, even after long shaking. In order to get rid of this impurity, the whole of the oil was shaken with water, filtered from the small quantity of undissolved oil, the filtrate evaporated to a small bulk on the water bath at a temperature of about 70°, and the residue allowed to stand over sulphuric acid in a vacuum until no further loss in weight occurred. Three analyses of the colourless, syrupy residue, obtained in two distinct experiments, gave the following numbers.



0.1007 gave 0.2110  $\text{CO}_2$  and 0.0748  $\text{H}_2\text{O}$ .  $\text{C} = 57.14$ ;  $\text{H} = 8.25$ .  
 0.1247 „ 0.2593  $\text{CO}_2$  „ 0.0938  $\text{H}_2\text{O}$ .  $\text{C} = 56.71$ ;  $\text{H} = 8.35$ .  
 0.1123 „ 0.2365  $\text{CO}_2$  „ 0.0853  $\text{H}_2\text{O}$ .  $\text{C} = 57.44$ ;  $\text{H} = 8.43$ .  
 $\text{C}_9\text{H}_{16}\text{O}_4$  requires  $\text{C} = 57.45$ ;  $\text{H} = 8.51$  per cent.

The *silver salt* of the acid, prepared by precipitating the slightly alkaline solution of the ammonium salt with silver nitrate, is a white, insoluble precipitate, which, after washing and drying at  $100^\circ$ , gave the following results on analysis.

0.2033 gave 0.2016  $\text{CO}_2$ , 0.0620  $\text{H}_2\text{O}$ , and 0.1090 Ag.

$\text{C} = 27.04$ ;  $\text{H} = 3.39$ ;  $\text{Ag} = 53.61$ .

0.2070 gave 0.2094  $\text{CO}_2$ , 0.0635  $\text{H}_2\text{O}$  and 0.0112 Ag.

$\text{C} = 27.58$ ;  $\text{H} = 3.40$ ;  $\text{Ag} = 53.72$ .

Additional silver determinations gave  $\text{Ag} = 53.87$ ,  $53.58$ , and  $53.75$ .

$\text{C}_9\text{H}_{14}\text{O}_4\text{Ag}_2$  requires  $\text{C} = 26.86$ ;  $\text{H} = 3.48$ ;  $\text{Ag} = 53.73$  per cent.

The neutral solution of the ammonium salt of this acid shows the following behaviour with reagents.

*Barium chloride*, no precipitate, even on boiling.

*Calcium chloride*, with strong solutions, a white, gelatinous precipitate but this dissolves readily in water.

*Copper sulphate*, a bluish-green, gelatinous precipitate, which becomes caseous on warming.

*Lead acetate*, a heavy, white, amorphous precipitate.

The *anhydride* of the acid was prepared by boiling the acid with excess of acetic anhydride for two days in a reflux apparatus, and fractionating the product under reduced pressure (35 mm.); the colourless oil thus obtained, which was far less viscid than the acid, boiled at  $185-190^\circ$ .

0.1345 gave 0.3142  $\text{CO}_2$  and 0.0994  $\text{H}_2\text{O}$ .  $\text{C} = 63.71$ ;  $\text{H} = 8.21$ .

0.1872 „ 0.4368  $\text{CO}_2$  „ 0.1382  $\text{H}_2\text{O}$ .  $\text{C} = 63.66$ ;  $\text{H} = 8.20$ .

$\text{C}_9\text{H}_{14}\text{O}_3$  requires  $\text{C} = 63.53$ ;  $\text{H} = 8.24$  per cent.

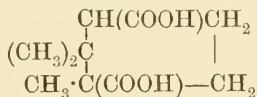
From the results given above, it is clear that the oil distilling at  $254-257^\circ$  (50 mm.) is a mixture of a large quantity of an acid of the formula  $\text{C}_9\text{H}_{16}\text{O}_4$  with a small quantity of an oil the nature of which we were not able to determine. It is very remarkable that this acid, which is capable of forming an anhydride, should not do so at the high temperature at which it was distilled.



## II.—*Experiments on the Synthesis of Camphoric Acid.* *Part I.*

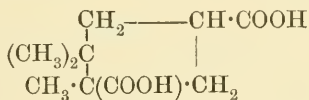
By WILLIAM HENRY BENTLEY and WILLIAM HENRY PERKIN, JUN.

DURING the course of a series of experiments on sulphocamphylic acid,  $\text{COOH} \cdot \text{C}_8\text{H}_{12} \cdot \text{SO}_3\text{H}$ , on which one of us has been engaged for a long time, many results have been obtained which are very difficult to understand if we assume that Bredt's formula for camphoric acid,



is correct.

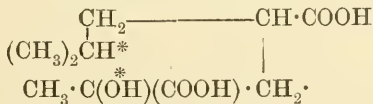
On the other hand, if this formula be slightly modified by altering the position of one of the carboxyl groups, so as to express the constitution of camphoric acid thus,



all the results obtained during the investigation on sulphocamphylic acid may be readily explained.

As, moreover, it appears that this formula is capable of accounting for all the other known reactions of camphoric acid, it seems highly probable that it may actually represent the constitution of camphoric acid.

In order, if possible, to decide this important point, experiments were made with the object of synthesising an acid of this constitution, the method adopted being to prepare, in the first place, an isobutyl-methylhydroxyglutaric acid of the formula



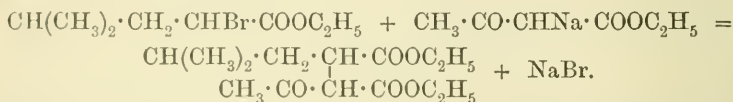
and then to endeavour to remove the elements of water at the points \*. It seemed probable that this might be effected from the consideration that the elimination of water in this way would give rise to a 5 carbon ring—the ring which is supposed to be capable of the most ready formation, and also on account of the probability that camphoric acid, which is such an exceedingly stable substance, would be very likely to be produced if the conditions necessary for its formation presented themselves.

We have been successful in preparing isobutylmethylhydroxyglutaric

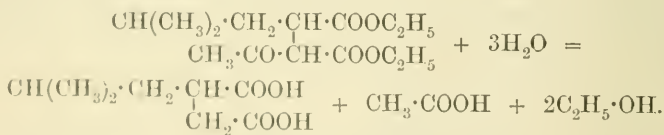
acid, but the elimination of water from this acid in the direction shown above has, so far, not been realised; it is to be hoped, however, that further experiments which are in progress may yet lead to the desired result.

The starting point in this investigation was isobutylacetic acid,  $\text{CH}(\text{CH}_3)_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{COOH}$ , which we prepared in considerable quantity in the usual way from ethylic isobutylmalonate by hydrolysis and subsequent distillation of the isobutylmalonic acid. When the product formed on treating this acid with phosphorus pentabromide and bromine was poured into alcohol, a very good yield of ethylic  $\alpha$ -bromisobutylacetate,  $\text{CH}(\text{CH}_3)_2 \cdot \text{CH}_2 \cdot \text{CHBr} \cdot \text{COOC}_2\text{H}_5$ , was obtained as a colourless oil boiling at  $100\text{--}103^\circ$  (17mm.).

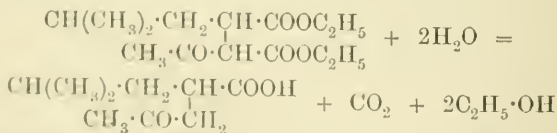
If now the sodium compound of ethylic acetoacetate be digested in alcoholic solution with this brominated ethereal salt, reaction takes place readily with elimination of sodium bromide, ethylic acetylisobutylsuccinate, a colourless oil boiling at  $160^\circ$  (25 mm.) being produced, according to the equation,



The hydrolysis of this ethereal salt by means of hydrochloric acid was next investigated, and after many experiments it was found that the course of the hydrolysis did not always go in the same direction, the nature of the products depending principally on the strength of the acid employed. If the hydrolysis is effected by boiling with dilute hydrochloric acid, the principal products of the reaction are isobutylsuccinic acid and acetic acid.



On the other hand, boiling with concentrated hydrochloric acid decomposes the ethereal salt in a different manner, isobutyllevulinic acid being produced.



Isobutyllevulinic acid, which is a viscid, odourless oil boiling at about  $190^\circ$  (30 mm.), shows all the properties of a ketonic acid, since, in ad-

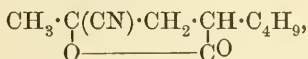
dition to dissolving in alkalis, it yields a well-defined *semicarbazone*,  $\text{NH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{N} : \text{C}(\text{CH}_3) \cdot \text{CH}_2 \cdot \text{CH}(\text{COOH}) \cdot \text{CH}_2 \cdot \text{CH}(\text{CH}_3)_2$ , melting at  $192^\circ$ . Its constitution is proved by the fact that when oxidised by bromine in the presence of potash, it gives an almost quantitative yield of isobutylsuccinic acid,



The next step was to investigate the action of hydrocyanic acid on isobutyllevulinic acid, and it was ultimately found that, if the conditions given in this paper are observed, addition readily takes place with formation of isobutylhydroxycyanovaleric acid.

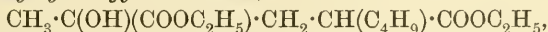


This hydroxycyanide is a crystalline substance which melts at  $95-96^\circ$ , and on distillation is decomposed with loss of water and formation of the corresponding lactone which melts at  $53^\circ$ ,

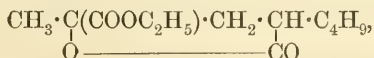


a behaviour which was to be expected, since the hydroxycyanide is at the same time a  $\gamma$ -hydroxy-acid.

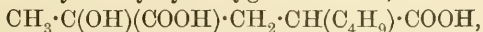
The hydrolysis of the hydroxycyanide was carried out by saturating its alcoholic solution with hydrogen chloride, and in this way an ethereal salt was obtained which was doubtless the ethereal salt of *isobutylmethylhydroxyglutaric acid*,



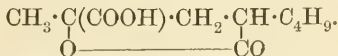
but if this ethereal salt be distilled under reduced pressure (17 mm.), an oil passes over at  $168^\circ$  which, on analysis, proved to be the ethylic salt of the lactone of isobutylmethylhydroxyglutaric acid,



alcohol having been eliminated during the distillation. From the ethylic salt, isobutylmethylhydroxyglutaric acid,



is readily obtained by hydrolysing it with alcoholic potash and precipitating the cold solution with hydrochloric acid; it is a beautifully crystalline substance which melts at  $134^\circ$  with elimination of water and formation of the lactone,



The latter, which is best prepared by treating the hydroxydibasic acid with acetyl chloride, is crystalline, and melts at about  $80^\circ$ . When dissolved in potash, it is converted into the potassium salt of the

hydroxy-acid, and this, on acidifying in the cold, yields the free acid, showing that this  $\gamma$ -hydroxy-acid is not so readily converted into its lactone as is the case with most  $\gamma$ -hydroxy-acids.

The following experiments were instituted in order, if possible, to obtain either camphoric acid or an isomeride by the elimination of water from isobutylmethylhydroxyglutaric acid in the manner indicated at the commencement of this paper, but so far we have been unable to obtain the desired result.

I. The diethylic salt of the acid, prepared from the silver salt by the action of ethylic iodide, was distilled under the ordinary pressure, when the whole passed over at  $290^{\circ}$  as a colourless oil; this, on analysis, was found to consist of the ethylic salt of the lactone of the hydroxy-acid, alcohol having been eliminated during the operation.

II. The diethylic salt was left in contact with excess of phosphorus pentoxide for eight days, and the product, after extraction with ether, was fractionated under the ordinary pressures; in this case, also, the distillate was found to consist of the ethylic salt of the lactone acid.

III. In order, if possible, to prevent the formation of the lactone, the hydroxy-dibasic acid was fused with potash at about  $300^{\circ}$ , at which temperature camphoric acid, if formed, would remain unattacked. It was, however, found that, during this experiment, the hydroxy-acid had en completely decomposed, isobutylsuccinic acid being produced.

IV. The carefully dried silver salt of the hydroxy-dibasic acid was submitted to distillation under reduced pressure. An oily distillate was obtained which, on refractionation, gave a large quantity of a fraction  $220\text{--}222^{\circ}$  (30 mm.); this, which solidified on standing, was found to be the lactone of the hydroxy-acid.

Several other substances of interest which were obtained during the course of this investigation are described in this paper.

#### *Isobutylacetic Acid*, $\text{CH}(\text{CH}_3)_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{COOH}$ .

This acid has already been prepared synthetically by the hydrolysis of isoamylic cyanide with alkalis (Frankland, Kolbe, *Annalen*, 65, 303), and also by the hydrolysis of ethylic isobutylacetoacetate with baryta (Rohn, *Annalen*, 1878, 190, 316); the isobutylacetic acid which was employed in this research was prepared from isobutylmalonic acid, a method which does not appear to have been described, and which we found to yield the acid in a very pure state.

Ethylic isobutylmalonate was prepared in the usual way by treating ethylic sodiomalonate with isobutylic bromide (compare Guthzeit, *Annalen*, 1881, 209, 236), and after careful fractionation\* the pure

\* During the fractionation, a small quantity of an oil of high boiling point, ethylic di-isobutyl malonate (see p. 61), is always obtained.

ethereal salt was hydrolysed by boiling with excess of alcoholic potash for four hours. After being mixed with water and freed from alcohol by evaporation, the residue was dissolved in a little water, acidified, and extracted six times with pure ether; the ethereal solution was then dried over calcium chloride, evaporated, and the residual crude isobutylmalonic acid decomposed by distillation. In this way, about 70 per cent. of the theoretical yield of pure isobutylacetic acid was readily obtained as a colourless, disagreeably-smelling oil boiling constantly at 200—201°.

0.1840 gave 0.4191  $\text{CO}_2$  and 0.1738  $\text{H}_2\text{O}$ .  $\text{C} = 62.12$ ;  $\text{H} = 10.48$ .

$\text{C}_5\text{H}_{11}\cdot\text{COOH}$  requires  $\text{C} = 62.07$ ;  $\text{H} = 10.35$  per cent.

*Ethyllic Bromisobutylacetate*,  $\text{CH}(\text{CH}_3)_2\cdot\text{CH}_2\cdot\text{CHBr}\cdot\text{COOC}_2\text{H}_5$ .—In order to prepare this, isobutylacetic acid (85 grams) was mixed with phosphorus pentabromide (127 grams), and after some time dry bromine (140 grams) was added in small quantities at a time, and the mixture heated at 50° for about 2 hours, until the evolution of hydrogen bromide had nearly ceased; the temperature was then raised to 100° in order to drive off the last traces of bromine. When cold, the product was poured into alcohol and the whole allowed to stand overnight. A large quantity of water was then added, the heavy oil which was precipitated was extracted with ether, and the ethereal solution, after being washed with sodium carbonate solution and with water, was dried; the ether was then distilled off, and the oily residue fractionated under reduced pressure. Pure ethylic bromisobutylacetate is thus readily obtained as a heavy, colourless, pleasant-smelling oil which boils at 100—103° (17 mm.) and has properties similar to other ethereal salts of  $\alpha$ -bromo-fatty acids. The yield is about 90 per cent. of the theoretical.

0.1522 gave 0.1280  $\text{AgBr}$ .  $\text{Br} = 35.78$ .

$\text{C}_4\text{H}_9\cdot\text{CHBr}\cdot\text{COOC}_2\text{H}_5$  requires  $\text{Br} = 35.87$  per cent.

*Ethyllic Acetylisobutylsuccinate*, 
$$\begin{array}{c} \text{CH}(\text{CH}_3)_2\cdot\text{CH}_2\cdot\text{CH}\cdot\text{COOC}_2\text{H}_5 \\ | \\ \text{CH}_3\cdot\text{CO}\cdot\text{CH}\cdot\text{COOC}_2\text{H}_5 \end{array}$$

This is produced by the interaction of ethylic  $\alpha$ -bromisobutylacetate with ethylic sodacetoacetate, as explained in the introduction of this paper. Sodium (11.5 grams) was dissolved in alcohol (130 grams), the solution mixed with ethylic acetoacetate (65 grams), ethylic bromisobutyl acetate (112 grams) added, and the mixture heated for 12—15 hours in a reflux apparatus on the water bath. The product, when cold, was mixed with water and extracted with ether, &c., the residue being fractionated under reduced pressure (25 mm.). The ethylic acetylisobutylsuccinate commences to distil at 140°, almost the whole



passing over between  $140^{\circ}$  and  $180^{\circ}$ ; a small quantity of oil boiling at  $200$ — $230^{\circ}$  was, however, obtained in each case, but this was not examined.

The fraction boiling at  $140$ — $180^{\circ}$  varies from 65—70 per cent. of the theoretical; a small portion of this, which was specially collected, distilled at about  $160^{\circ}$  (25 mm.) and gave the following numbers on analysis.

0.1188 gave 0.2660  $\text{CO}_2$  and 0.0935  $\text{H}_2\text{O}$ .  $\text{C} = 61.06$ ;  $\text{H} = 8.74$ .

Ethylis acetylisobutylsuccinate requires  $\text{C} = 61.76$ ;  $\text{H} = 8.82$  per cent.

Other analyses gave a similar result, and it was subsequently ascertained that the somewhat low numbers found were due to the substance containing traces of bromine (see p. 65).

*Hydrolysis of Ethylis Acetylisobutylsuccinate. Formation of Isobutylsuccinic Acid,*  $\text{CH}(\text{CH}_3)_2 \cdot \text{CH}_2 \cdot \underset{\text{CH}_2 \cdot \text{COOH}}{\text{CH}} \cdot \text{COOH}$ , *and of  $\alpha$ -Isobutyllevulinic Acid,*  $\text{CH}(\text{CH}_3)_2 \cdot \text{CH}_2 \cdot \underset{\text{CH}_3 \cdot \text{CO} \cdot \text{CH}_2}{\text{CH}} \cdot \text{COOH}$ .

a. The hydrolysis of ethylis acetylisobutylsuccinate with dilute hydrochloric acid yields *isobutylsuccinic acid*.

The fraction of the ethereal salt boiling at about  $150$ — $155^{\circ}$  (20 mm.) and weighing 48 grams was digested for about 15 hours in a reflux apparatus with 220 grams of dilute hydrochloric acid (1 acid: 2 of water), but even after boiling for this length of time, comparatively little of the ethereal salt had been hydrolysed. The liquid was accordingly extracted several times with ether, and the ethereal solution repeatedly shaken with small quantities of sodium carbonate; the aqueous solution, after being separated from the ether, was acidified and again extracted with ether. This second ethereal solution, after being dried and evaporated, left a yellowish oil which soon solidified. The crude crystalline mass, after being left in contact with porous porcelain, was purified by crystallisation from water, when it separated in colourless prisms which melted at  $109^{\circ}$ , and gave off water at about  $150^{\circ}$ .

0.1172 gave 0.2368  $\text{CO}_2$  and 0.0854  $\text{H}_2\text{O}$ .  $\text{C} = 55.10$ ;  $\text{H} = 8.09$ .

$\text{C}_8\text{H}_{14}\text{O}_4$  requires  $\text{C} = 55.17$ ;  $\text{H} = 8.04$  per cent.

It seemed likely that this acid was isobutylsuccinic acid, identical with the acid which Demarçay (*Ann. Chim. Ph.*, [v], 20, 492) obtained by the reduction of isobutylyfumaric acid, and for which he gives the melting point  $103$ — $104^{\circ}$ . As, however, it was important to be quite sure of the identity of our acid, we prepared isobutylsuccinic acid



by a method which left no doubt as to its constitution, namely, the action of ethylic monochloracetate on ethylic isobutylsodiummalonate; the acid prepared in this way melted at  $109^{\circ}$ , and has all the properties of that obtained by the hydrolysis of ethylic acetylisobutylsuccinate.

The *anilic acid*,  $\text{CH}(\text{CH}_3)_2 \cdot \text{CH}_2 \cdot \underset{\text{CH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_6\text{H}_5}{\text{CH}} \cdot \text{COOH}$  (1), was prepared from both specimens by the following method. The acid (1 gram) was heated with a few grams of acetyl chloride for half an hour, the liquid placed over solid potash in a vacuum desiccator until the excess of acetyl chloride had been removed, and the oily residue dissolved in a little benzene and mixed with aniline (1 gram); the crystals which soon separated on standing were collected, dried on a porous plate, and purified by crystallisation from benzene mixed with a little alcohol; the isobutylsuccinanilic acid was thus obtained in glistening plates melting at  $138-139^{\circ}$ .

0.1792 gave 9.1 c.c. nitrogen at  $17^{\circ}$  and 745 mm.  $N = 5.82$ .

$\text{C}_{14}\text{H}_{19}\text{NO}_3$  requires  $N = 5.62$  per cent.

The same anilic acid was obtained from both preparations of isobutylsuccinic acid; subsequently it was also discovered that isobutylsuccinic acid is formed when ethylic acetylisobutylsuccinate is hydrolysed by heating it with a mixture of sulphuric acid, acetic acid, and a little water.

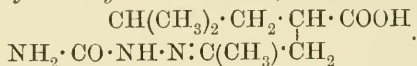
*b.* The hydrolysis of ethylic acetylisobutylsuccinate with strong hydrochloric acid results mainly in the formation of *isobutyllevulinic acid*. After numerous experiments had been tried in order to ascertain the most favourable conditions for the formation of isobutyllevulinic acid, the following method was adopted. Ethylic acetylisobutylsuccinate was digested in a reflux apparatus with about four times its volume of concentrated hydrochloric acid for 10 hours, but a portion only of the ethereal salt was hydrolysed. The product was shaken several times with ether, and the isobutyllevulinic acid separated from the unchanged ethereal salt, by extracting the ethereal solution with strong sodium carbonate solution, the ethylic salt recovered from the ethereal solution by evaporation being again submitted to hydrolysis as before; these operations were repeated until the concentrated hydrochloric acid had no further action on the oily layer (see p. 65). The combined sodium carbonate extracts were then acidified and extracted repeatedly with ether, &c., and the oil thus obtained was purified by distillation under reduced pressure; almost the whole distilled between  $160^{\circ}$  and  $180^{\circ}$  (20 mm.), and consisted for the most part of the ketonic acid, as the following analysis shows.

0.101 gave 0.2278  $\text{CO}_2$  and 0.0770  $\text{H}_2\text{O}$ .  $C = 61.51$ ;  $H = 8.47$ .

Isobutyllevulinic acid,  $\text{C}_9\text{H}_{16}\text{O}_3$ , requires  $C = 62.79$ ;  $H = 9.30$  per cent.

From this crude product, pure isobutyllevulinic acid may be readily obtained by converting it into the semicarbazone, purifying this, and subsequently decomposing the pure semicarbazone by means of hydrochloric acid.

*Semicarbazone of Isobutyllevulinic Acid,*



—This is readily prepared by adding the crude ketonic acid (30 grams), dissolved in a little alcohol, to a strong solution of semicarbazide hydrochloride (20 grams) and sodium acetate (32 grams), stirring the mixture vigorously, and heating to boiling for a few minutes; on cooling, a crystalline mass separates, which is collected, dried on a porous plate, and recrystallised from 70 per cent. alcohol; it is thus obtained in glistening plates melting at 192° with decomposition.

0.1594 gave 25.4 c.c. nitrogen at 16° and 762 mm.  $N = 18.63$ .

$\text{C}_{10}\text{H}_{19}\text{N}_3\text{O}_3$  requires  $N = 18.34$  per cent.

The semicarbazone of isobutyllevulinic acid is almost insoluble in water, benzene, and light petroleum, but dissolves readily in alcohol and in acetic acid. It is readily decomposed by hydrochloric acid into semicarbazide hydrochloride and isobutyllevulinic acid.

The pure semicarbazone (20 grams) was heated on the water bath with hydrochloric acid (30 c.c. of sp. gr. 1.1) and water (30 c.c.) until the crystals had been entirely decomposed and changed to an oil; the product was then extracted with ether in the usual way, and the oily residue fractionated under reduced pressure. The whole distilled at about 190° (30 mm.) as a colourless oil, consisting of pure isobutyllevulinic acid.

0.1150 gave 0.2646  $\text{CO}_2$  and 0.0964  $\text{H}_2\text{O}$ .  $C = 62.75$ ;  $H = 9.31$ .

$\text{C}_9\text{H}_{16}\text{O}_3$  requires  $C = 62.79$ ;  $H = 9.30$  per cent.

*Oxidation of Pure Isobutyllevulinic Acid by means of Potassium Hypobromite. Formation of Isobutylsuccinic Acid.*

It has already been pointed out (p. 50) that isobutylsuccinic acid is formed in considerable quantity during the hydrolysis, by means of dilute hydrochloric acid, of that portion of the product of the action of ethylic bromoisobutylacetate on ethylic sodacetoacetate which boils at 150—155° (20 mm.), and the formation of this acid proves that this oily product contains ethylic acetoisobutylsuccinate.

It seemed, however, quite likely that this oil might contain a second isomeric constituent formed by the elimination of hydrogen bromide from ethylic bromisobutylacetate, and the subsequent condensation of the ethylic  $\beta$ -isopropylacrylate  $\text{CH}(\text{CH}_3)_2 \cdot \text{CH} : \text{CH} \cdot \text{COOC}_2\text{H}_5$ ,

thus formed, with the ethylic acetoacetate, a series of reactions which have been repeatedly noticed in cases analogous to the above.

Since, then, it was possible that the substance we call isobutyllevulinic acid might have been derived from this second constituent, it became necessary, before using this acid for synthetical work, to be quite sure as to its constitution, and this was proved by oxidising the acid to isobutylsuccinic acid by means of potassium hypobromite.

Some of the ketonic acid which had been regenerated from the pure carbazone was dissolved in a considerable excess of strong potash solution and bromine added until, on standing for an hour, the solution liberated iodine from a solution of potassium iodide. The first drop of bromine produced a turbidity in the alkaline solution and then an oil separated which ultimately solidified; this, which consisted of carbon tetrabromide, was removed by filtration, the solution acidified with hydrochloric and sulphurous acids, and the oily acid extracted with ether. After distilling off the ether, an almost colourless oil was left, which showed no signs of solidifying; when, however, it had been dissolved in dilute sodium carbonate, the solution boiled with animal charcoal, filtered, and the filtrate acidified and allowed to stand for some days in a cold place, the acid was deposited in a semi-solid state, and in contact with porous porcelain became quite hard. After being purified by recrystallisation from water, pure isobutylsuccinic acid was obtained in colourless plates melting at  $109^{\circ}$ .

0.1364 gave 0.2748  $\text{CO}_2$  and 0.099  $\text{H}_2\text{O}$ .  $\text{C} = 54.95$ ;  $\text{H} = 8.06$ .

$\text{C}_8\text{H}_{14}\text{O}_4$  requires  $\text{C} = 55.17$ ;  $\text{H} = 8.04$  per cent.

The identity of this acid was further demonstrated by converting it into isobutylsuccinanilic acid and isobutylsuccinanil, which were found to be identical with the substances obtained from synthetical isobutylsuccinic acid (see p. 51).

*Action of Hydrogen Cyanide on  $\alpha$ -Isobutyllevulinic Acid. Formation of  $\alpha$ -Isobutyl- $\gamma\gamma$ -hydroxycyanovaleric Acid,*  
 $\text{CH}_3 \cdot \text{C}(\text{OH})(\text{CN}) \cdot \text{CH}_2 \cdot \text{CH}(\text{C}_4\text{H}_9) \cdot \text{COOH}.$

In the first experiments on the action of hydrogen cyanide on isobutyllevulinic acid, the pure ketonic acid prepared from the semicarbazone was employed, and it was then found that this reaction gave rise to a solid hydroxycyanide and an oil containing much nitrogen; the latter was at first thought to be a stereoisomeric modification of the solid cyanide.

Subsequently, when it was found that it was unnecessary to employ such carefully purified ketonic acid, the usual method of procedure was as follows.

Isobutyllevulinic acid (b. p. 185—195° at 30 mm.), in quantities of 30 grams, was mixed with water (45 grams), and pure potassium cyanide (18 grams) added in small quantities at a time, the whole being cooled in a freezing mixture during the operation. The mixture, which soon became almost solid, was allowed to stand for about an hour, and concentrated hydrochloric acid (12 grams) then added, care being taken that the temperature did not rise much above 0°. After 2 hours, more hydrochloric acid (30 grams) was added, and the whole kept at 0° for about 20 hours. At the end of this time, it was seen that the oil which separated on adding the second quantity of hydrochloric acid had almost completely solidified; this semi-solid mass, after being washed and left in contact with porous porcelain until quite free from oily impurity, was recrystallised from dilute methylic alcohol, from which it separated in the form of beautiful, colourless needles melting at 95—96°. For analysis, the substance was dried over sulphuric acid in a vacuum, as it decomposes even below its melting point when heated in a water bath.

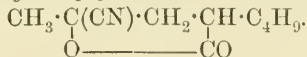
0.1220 gave 0.2484 CO<sub>2</sub> and 0.0980 H<sub>2</sub>O. C = 55.54; H = 8.92.

0.2356 „ 13.2 c.c. nitrogen at 14° and 764 mm. N = 6.63.

C<sub>10</sub>H<sub>17</sub>NO<sub>3</sub> + H<sub>2</sub>O requires C = 55.30; H = 8.75; N = 6.45 per cent.

Isobutylhydroxycyanovaleric acid appears, therefore, to crystallise from dilute methylic alcohol with 1H<sub>2</sub>O. It is readily soluble in acetic acid, alcohol and hot water, but only sparingly in benzene, chloroform or light petroleum; if warmed for some time with hot water, it decomposes, yielding hydrocyanic acid and an oil which is possibly regenerated isobutyllevulinic acid.

*Lactone of Isobutylhydroxycyanovaleric Acid,*



When pure isobutylhydroxycyanovaleric acid is distilled under reduced pressure (40 mm.), water is first eliminated, and then the temperature rises rapidly to 175°, nearly the whole of the residue distilling between 178° and 180° (40 mm.) as a colourless oil; this, however, is not the pure lactone, as is shown by the following analysis. Found, N = 5.75 per cent.; C<sub>10</sub>H<sub>15</sub>NO<sub>2</sub> requires N = 7.73 per cent.

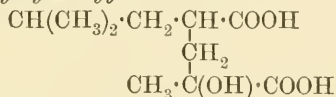
This oil, which appeared to contain some isobutyllevulinic acid, on long standing at 0°, deposited colourless plates which, after being spread on porous porcelain until quite dry and then washed with light petroleum, melted at 40—50°. The analysis now gave the correct numbers.

0.1550 gave 10.1 c.c. nitrogen at 22° and 760 mm.. N = 7.45.

C<sub>10</sub>H<sub>15</sub>NO<sub>2</sub> requires N = 7.73 per cent.

This substance, which is evidently the lactone of isobutylhydroxycyanovaleric acid, melts at 53°. It crystallises in beautiful, glistening plates, and is readily soluble in alcohol and ether, but almost insoluble in water. It is insoluble in cold soda solution, and when warmed the crystals melt and swim about in the hot alkaline solution as an oil.

*α-Isobutyl-α<sub>1</sub>α<sub>1</sub>-methylhydroxyglutaric Acid.*



This acid is formed by the hydrolysis of isobutylhydroxycyanovaleric acid by means of hydrochloric acid, the method which was adopted for the hydrolysis and isolation of the acid being as follows. Absolute alcohol (60 grams) was saturated with dry hydrogen chloride, and to the cold liquid the solid cyano-acid (30 grams) was added, and the mixture then allowed to stand at the ordinary temperature for two days. At the end of this time, a considerable quantity of ammonium chloride had separated, and the process appeared to be complete; in order, however, to make sure that the whole of the cyano-acid had been hydrolysed, the product was heated on the water bath for 4 hours before being worked up. The whole was then cooled, diluted with water, and the oily ethereal salt which separated extracted with ether; this was washed, dried, and evaporated, and the oily residue purified by fractionation under reduced pressure. In this way, a colourless oil was obtained, which distilled almost constantly at 168° (17 mm.).

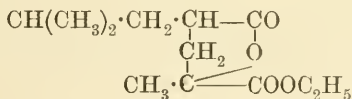
0.1152 gave 0.2666 CO<sub>2</sub> and 0.0930 H<sub>2</sub>O. C = 63.11; H = 8.97.

0.1080 „ 0.2502 CO<sub>2</sub> „ 0.0874 H<sub>2</sub>O. C = 63.18; H = 8.99 per cent.

C<sub>12</sub>H<sub>20</sub>O<sub>4</sub> requires C = 63.16; H = 8.77.

C<sub>14</sub>H<sub>26</sub>O<sub>5</sub> requires C = 61.31; H = 9.48 per cent.

This substance is therefore not the ethereal salt of isobutylmethylhydroxyglutaric acid itself (C<sub>14</sub>H<sub>26</sub>O<sub>5</sub>), but of the lactone of this acid (C<sub>12</sub>H<sub>20</sub>O<sub>4</sub>), that is,



It is a colourless oil of faint odour, and distils without decomposition at about 290° under the ordinary pressures (see p. 57). In order to prepare the dibasic acid from this ethereal salt, the pure substance (25 grams) was added to a solution of potash (20 grams) in pure ethylic alcohol, and the solution heated in a reflux apparatus on the water



bath. In a short time, a solid potassium salt began to separate, which increased rapidly in quantity until the whole, after about an hour and a half, had become quite thick; the mass was then cooled, the solid crystalline precipitate collected with the aid of the pump, washed with alcohol, and dried at  $100^{\circ}$ .

This substance, which proved to be the potassium salt of an organic acid, was dissolved in water, and the solution, after filtering, was cooled with ice and carefully acidified with hydrochloric acid, when a beautifully crystalline acid was precipitated; this was collected, washed, dried, and analysed, with the following result.

0.1164 gave 0.2348  $\text{CO}_2$  and 0.0876  $\text{H}_2\text{O}$ .  $\text{C} = 55.01$ ;  $\text{H} = 8.36$ .

$\text{C}_{10}\text{H}_{18}\text{O}_5$  requires  $\text{C} = 55.04$ ;  $\text{H} = 8.26$  per cent.

The *silver salt* of the acid precipitated from a neutral solution of the ammonium salt is a white, amorphous, very insoluble substance. On analysis, it gave the following result.

0.1008 gave 0.0508 Ag.  $\text{Ag} = 50.39$ .

$\text{C}_{10}\text{H}_{16}\text{Ag}_2\text{O}_5$  requires  $\text{Ag} = 50.00$  per cent.

These analyses prove that the acid obtained in this way is *isobutylmethylhydroxyglutaric acid*. When heated in a capillary tube, it softens at  $128^{\circ}$  and melts at  $134^{\circ}$  with evolution of gas, due, no doubt, to the elimination of water and formation of the lactone (p. 58). It is sparingly soluble in cold, but dissolves in warm water; if the solution, however, be boiled, an oil separates, a change which is obviously due to lactone formation. The dibasic acid is sparingly soluble in cold benzene and light petroleum, but dissolves readily in alcohol and acetic acid. It may be obtained in a beautifully crystalline condition by dissolving it in much warm ether, distilling off the ether until crystals begin to separate, and then allowing the solution to stand, when the greater part of the acid separates in beautiful, glistening, silky plates.

*Ethylic Isobutylmethylhydroxyglutarate*,  $\text{OH} \cdot \text{C}_8\text{H}_{15}(\text{COOC}_2\text{H}_5)_2$ .—In order to prepare this, experiments were first tried on the action of hydrogen chloride on the alcoholic solution of the acid, but as the ethereal salt which was formed proved on investigation to be the ethylic salt of the lactonic acid, we were forced to make the ethylic salt of the dibasic acid from the silver salt by the action of ethylic iodide.

The dry silver salt of the dibasic acid (10 grams) was heated in a reflux apparatus with ethylic iodide (10 grams) and pure dry ether for 2 hours on the water bath; the silver iodide was then filtered off, washed with ether, the ethereal solution evaporated, and the residual almost colourless oil left in a vacuum desiccator over sulphuric



acid for about a week. The analysis of the oil gave numbers showing that it was the ethereal salt of the dibasic acid.

0.148 gave 0.3297  $\text{CO}_2$  and 0.126  $\text{H}_2\text{O}$ .  $\text{C} = 60.72$ ;  $\text{H} = 9.46$ .

$\text{OH} \cdot \text{C}_8\text{H}_{15}(\text{COOC}_2\text{H}_5)_2$  requires  $\text{C} = 61.31$ ;  $\text{H} = 9.48$  per cent.

When this oil is distilled under the ordinary pressure, alcohol is eliminated and a colourless, oily ethereal salt distils remarkably constantly at  $290^\circ$  with scarcely any decomposition; this, on analysis, proved to be the ethylic salt of the lactonic acid.

0.1362 gave 0.3136  $\text{CO}_2$  and 0.1116  $\text{H}_2\text{O}$ .  $\text{C} = 62.79$ ;  $\text{H} = 9.10$ .

$\text{COOC}_2\text{H}_5 \cdot \text{C}_8\text{H}_{15} \begin{smallmatrix} \text{O} \\ \diagup \quad \diagdown \\ \text{C} \end{smallmatrix}$  requires  $\text{C} = 63.16$ ;  $\text{H} = 8.77$  per cent.

This, after being hydrolysed by boiling with excess of potash or methylic alcohol, was diluted with water, evaporated to dryness, and the residue, dissolved in a little water, was cooled, and acidified, when the colourless crystalline hydroxydibasic acid was precipitated.

0.1280 gave 0.2572  $\text{CO}_2$  and 0.0960  $\text{H}_2\text{O}$ .  $\text{C} = 54.80$ ;  $\text{H} = 8.33$ .

$\text{C}_{10}\text{H}_{18}\text{O}_5$  requires  $\text{C} = 55.04$ ;  $\text{H} = 8.26$  per cent.

In a preliminary experiment, in which less alkali was used, some of the ethereal salt on hydrolysis yielded a solid melting at  $78^\circ$ , which evidently consisted of the lactonic acid produced by direct hydrolysis.

*Action of Phosphorus Pentoxide on Ethylic Isobutylmethylhydroxyglutarate.*—As stated in the introduction, this experiment was instituted with the object of eliminating water from the ethereal salt, and of thus forming a closed chain, but the reaction evidently proceeds differently, alcohol being eliminated and the ethereal salt of the lactonic acid formed. The diethylic salt (5 grams) was mixed with a large excess of phosphorus pentoxide and allowed to stand in a desiccator over phosphorus pentoxide for 8 days; the gelatinous mass thus formed was then mixed with water, the oil which separated extracted with ether, the ethereal solution washed with sodium carbonate, dried over calcium chloride, and evaporated. The oily residue, after standing for 7 days over sulphuric acid in a vacuum desiccator, was analysed.

0.1434 gave 0.3356  $\text{CO}_2$  and 0.1196  $\text{H}_2\text{O}$ .  $\text{C} = 63.82$ ;  $\text{H} = 9.26$ .

On distillation under the ordinary pressure, nearly the whole passed over at  $290$ — $292^\circ$ , and on analysis and further examination it proved to be the ethylic salt of the lactonic acid.

0.1290 gave 0.2976  $\text{CO}_2$  and 0.1060  $\text{H}_2\text{O}$ .  $\text{C} = 62.91$ ;  $\text{H} = 9.13$ .

$\text{COOC}_2\text{H}_5 \cdot \text{C}_8\text{H}_{15} \begin{smallmatrix} \text{O} \\ \diagup \quad \diagdown \\ \text{C} \end{smallmatrix}$  requires  $\text{C} = 63.16$ ;  $\text{H} = 8.77$  per cent.

From this ethereal salt, by hydrolysis, both the lactonic acid and the dibasic acid were obtained, and the latter was analysed.

0.1024 gave 0.2064  $\text{CO}_2$  and 0.0767  $\text{H}_2\text{O}$ .  $\text{C} = 54.97$ ;  $\text{H} = 8.33$ .

$\text{C}_{10}\text{H}_{18}\text{O}_5$  requires  $\text{C} = 55.04$ ;  $\text{H} = 8.26$  per cent.

There can therefore be no doubt that the oily ethereal salt was simply the ethereal salt of the lactonic acid.

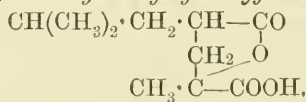
*Fusion of Isobutylmethylhydroxyglutaric Acid with Potash.*—This experiment was made in the hope that elimination of water might take place at the temperature of fusion with formation of a closed ring, which would probably be very stable, since camphoric acid itself is hardly attacked by fused potash at  $300^\circ$ . About 5 grams of the pure acid was fused with potash at  $220$ – $230^\circ$  for half an hour; the melt was then dissolved in water, and the clear solution acidified and extracted with ether. On evaporating the ether, an oil was left which, on standing for some days at  $0^\circ$ , gradually became nearly solid; it was then placed on porous porcelain and subsequently crystallised from water. The crystalline acid, melting at  $108$ – $109^\circ$ , thus obtained, proved to be isobutylsuccinic acid.

0.1219 gave 0.2472  $\text{CO}_2$  and 0.0892  $\text{H}_2\text{O}$ .  $\text{C} = 55.25$ ;  $\text{H} = 8.12$ .

$\text{C}_8\text{H}_{14}\text{O}_4$  requires  $\text{C} = 55.17$ ;  $\text{H} = 8.04$  per cent.

This experiment was repeated several times under different conditions, but isobutylsuccinic acid was formed in all cases.

*Lactone of Isobutylmethylhydroxyglutaric Acid,*



This lactone may be obtained from the hydroxydibasic acid in several ways, but we found that treating the acid with acetyl chloride yielded the best results. The pure hydroxydibasic acid boiled for a few minutes with a little pure acetyl chloride and then allowed to evaporate in a vacuum desiccator over solid potash, deposited prismatic crystals on standing overnight. These were collected, drained on a porous plate until quite dry, and then analysed without further purification.

0.1200 gave 0.2636  $\text{CO}_2$  and 0.0882  $\text{H}_2\text{O}$ .  $\text{C} = 59.91$ ;  $\text{H} = 8.16$ .

$\text{C}_{10}\text{H}_{16}\text{O}_4$  requires  $\text{C} = 60.00$ ;  $\text{H} = 8.00$  per cent.

The lactone of isobutylmethylhydroxyglutaric acid melts at about  $80^\circ$ , dissolves readily in alcohol and acetic acid, but is nearly insoluble in cold benzene, light petroleum, and water. When left in contact with water at about  $60^\circ$ , it gradually dissolves, probably with forma-

tion of the hydroxy-dibasic acid; in alkalis, it dissolves readily, and if the solutions are precipitated at once by hydrochloric acid, the lactone separates unchanged. If, however, the lactone is heated with excess of alkali for some time, and the solution then cooled with ice and cautiously acidified, the precipitate consists of the hydroxy-dibasic acid.

*Investigation of the Liquid Formed during the Action of Hydrogen Cyanide on Isobutyllevulinic Acid.*

It has already been stated that isobutyllevulinic acid reacts with hydrogen cyanide with formation of isobutylhydroxycyanovaleric acid, but the yield of the latter is not more than 50–60 per cent. of the theoretical, owing to the fact that some oily substance is always obtained at the same time; this is absorbed by the porous plates during the process of purification of the solid nitrile, and as it seemed possible that the examination of this oil might yield interesting results, these plates were broken up and extracted with ether in a Soxhlet apparatus. On distilling off the ether from the extract, a thick, dark brown oil containing nitrogen was left, and with this the following experiments were made.

*Behaviour of the Oil on Distillation.*—About one-third of the oil was distilled under reduced pressure (30 mm.), when, after a little water had come over, the temperature rose rapidly to  $140^{\circ}$ , most of the oil distilling at  $175$ – $185^{\circ}$ .

*Etherification of the Crude Oil.*—The crude, dark brown oil was dissolved in alcohol, the alcoholic solution saturated with hydrogen chloride, and the mixture left in the cold for two days, during which time a considerable quantity of ammonium chloride separated. The liquid was then heated in a reflux apparatus for one hour, diluted with water, and the oil which separated extracted with ether; the ethereal solution, after being washed with water and with sodium carbonate solution, dried over calcium chloride, and the ether distilled off, left an oil which was distilled under reduced pressure (25 mm.); almost the whole passed over between  $140^{\circ}$  and  $200^{\circ}$ , by far the larger portion at  $150$ – $160^{\circ}$ . The latter fraction gave the following results on analysis.

0.1170 gave 0.2810  $\text{CO}_2$  and 0.0992  $\text{H}_2\text{O}$ . C = 65.50; H = 9.41.

0.1285 „ 0.3102  $\text{CO}_2$  „ 0.1132  $\text{H}_2\text{O}$ . C = 65.84; H = 9.80.

Ethyl isobutyllevulinate,  $\text{C}_{11}\text{H}_{20}\text{O}_3$ , requires C = 66.0; H = 10.0 p. cent.

As this oil on hydrolysis gave a liquid acid which, with semicarbazide hydrochloride yielded a semicarbazone melting approximately at  $185^{\circ}$ , there can be no doubt that it is ethyl isobutyllevulinate, and this experiment shows that the original brown oil either contained

isobutyllevulinic acid, or that the latter had been produced by the action of hydrochloric acid on the hydroxycyanide contained in the oil.

A remarkable result was obtained in an experiment in which some of the fraction 150—160° (25 mm.) was boiled with water for four days in a reflux apparatus, as at the end of this time almost the whole had been converted into a solid crystalline substance. This after being washed with water and allowed to remain in contact with porous porcelain until quite free from oil, was purified by recrystallisation from 70 per cent. acetic acid, from which it separated in beautiful, rhombic crystals melting at 175—180°.

0.1230 gave 0.2980 CO<sub>2</sub> and 0.1050 H<sub>2</sub>O. C=66.07; H=9.48.

0.1210 „ 0.2942 CO<sub>2</sub> „ 0.1030 H<sub>2</sub>O. C=66.31; H=9.45.

C<sub>18</sub>H<sub>30</sub>O<sub>5</sub> requires C=66.28; H=9.20 per cent.

This acid is readily soluble in alcohol and acetic acid; but almost insoluble in water and light petroleum. It dissolves readily in dilute solutions of alkalis or alkali carbonates.

The *silver salt*, C<sub>18</sub>H<sub>29</sub>AgO<sub>5</sub>, was prepared from a slightly alkaline solution of the ammonium salt; it is a white, amorphous precipitate, which was analysed after washing and drying.

0.1230 gave 0.2236 CO<sub>2</sub>, 0.0770 H<sub>2</sub>O, and 0.0302 Ag. C=49.57; H=6.95; Ag=24.55.

C<sub>18</sub>H<sub>29</sub>AgO<sub>5</sub> requires C=49.88; H=6.69; Ag=24.94 per cent.

It is evident, therefore, that the substance C<sub>18</sub>H<sub>30</sub>O<sub>5</sub> is a monobasic acid, and it seems likely that it is formed by the elimination of water from two molecules of isobutyllevulinic acid, thus,



We have obtained no clue to the constitution of the acid, nor has any attempt been made to prepare the acid from pure isobutyllevulinic acid by boiling with water.

The higher fraction of the ethereal salt prepared as described above by the etherification of the crude brown oil, and which boiled at 170—190° (25 mm.), was hydrolysed by potash in the usual way. The acid which was thus obtained remained liquid for a long time, but after being in an exhausted desiccator for some weeks it had become semi-solid. The crude mass, spread on porous porcelain, was left until the crystals had become quite white; they were then dissolved in benzene, and the solvent allowed to evaporate slowly. The crystalline mass thus obtained, after drying on porous porcelain, gave the following results on analysis.

0.1168 gave 0.2564  $\text{CO}_2$  and 0.0852  $\text{H}_2\text{O}$ .  $\text{C} = 59.87$ ;  $\text{H} = 8.10$ .

$\text{C}_{10}\text{H}_{16}\text{O}_4$  requires  $\text{C} = 60.00$ ;  $\text{H} = 8.00$  per cent.

As this substance melts at  $75-80^\circ$ , it is evidently the lactone of isobutylmethylhydroxyglutaric acid (p. 58).

The crude brown oil so often referred to above may then very probably be simply a solution of some isobutylhydroxycyanovaleric acid in a considerable quantity of unchanged isobutyllevulinic acid, and, so far, there is no evidence of two stereoisomeric hydroxycyanides being produced by the action of hydrogen cyanide on isobutyllevulinic acid.

*Ethylic Di-isobutylmalonate*,  $[\text{CH}(\text{CH}_3)_2 \cdot \text{CH}_2]_2\text{C}(\text{COOC}_2\text{H}_5)_2$ .

During the preparation of ethylic isobutylmalonate, varying quantities of an ethereal salt boiling at about  $240-260^\circ$  were always obtained, and this, on examination, proved to be ethylic di-isobutylmalonate. As this substance, or rather the di-isobutyl acetic acid prepared from it, was required for some synthetical work which is in progress, we have investigated the matter carefully, and give here a description of our experiments, instead of publishing them in a separate paper. The ethylic di-isobutylmalonate employed for this purpose was partly that obtained as a bye-product in the preparation of ethylic isobutylmalonate, but the bulk of it was specially prepared in the following way.

Sodium (4.6 grams) was dissolved in absolute alcohol (55 grams) and mixed with ethylic isobutylmalonate (45 grams), isobutyl bromide (30 grams) was then added, and the whole heated in a reflux apparatus on the water bath for several hours. The alcohol was distilled off, water was added, and the product extracted three times with ether; the ethereal solution, after being washed with water, was dried over calcium chloride, the ether distilled off, and the residue purified by fractionation at the ordinary pressure.

In this way, ethylic di-isobutylmalonate (43 grams) was obtained as a thick, colourless oil boiling at  $245-255^\circ$ . Analysis.

0.0994 gave 0.2404  $\text{CO}_2$  and 0.0912  $\text{H}_2\text{O}$ .  $\text{C} = 65.96$ ;  $\text{H} = 10.19$ .

$(\text{C}_4\text{H}_9)_2\text{C}(\text{COOC}_2\text{H}_5)_2$  requires  $\text{C} = 66.17$ ;  $\text{H} = 10.29$  per cent.

*Di-isobutylmalonic Acid*,  $[\text{CH}(\text{CH}_3)_2 \cdot \text{CH}_2]_2\text{C}(\text{COOH})_2$ .

This acid is readily obtained by hydrolysing its ethylic salt with potash. Caustic potash (25 grams), dissolved in 90 per cent. alcohol, was mixed with ethylic di-isobutylmalonate (40 grams), and the whole heated on the water bath for 3 hours; the product was then diluted with water, evaporated until quite free from alcohol, acidified,



and extracted with pure ether. The ethereal solution, after being dried over calcium chloride and evaporated, gave an oily residue which solidified only very slowly, even when placed in a vacuum desiccator over sulphuric acid. After 14 days, the solid acid was pressed on porous plates in order to remove oily matter, and then purified by recrystallisation from light petroleum (b. p. 80—90°), when it was obtained in thick prisms melting at 145—150° with evolution of gas.

0.1054 gave 0.2352 CO<sub>2</sub> and 0.0884 H<sub>2</sub>O. C = 60.86; H = 9.32.

(C<sub>4</sub>H<sub>9</sub>)<sub>2</sub>C(COOH)<sub>2</sub> requires C = 61.11; H = 9.26 per cent.

Di-isobutylmalonic acid is almost insoluble in water and benzene, but dissolves readily in alcohol and in hot light petroleum (b. p. 80—90°); it is only sparingly soluble in cold light petroleum.

*Di-isobutylacetic Acid*, [CH(CH<sub>3</sub>)<sub>2</sub>·CH<sub>2</sub>]<sub>2</sub>CH·COOH, and its Derivatives.

In order to prepare this acid, crude di-isobutylmalonic acid was heated until carbon dioxide was no longer evolved, and it was then distilled. From the distillate, by fractional distillation, pure di-isobutylacetic acid was readily obtained as a viscid, colourless oil, of feeble odour, and boiling at 225—230° (730 mm.).

0.1004 gave 0.2560 CO<sub>2</sub> and 0.1050 H<sub>2</sub>O. C = 69.54; H = 11.61.

C<sub>10</sub>H<sub>20</sub>O<sub>2</sub> requires C = 69.77; H = 11.62 per cent.

*Di-isobutylacetyl chloride*, CH(C<sub>4</sub>H<sub>9</sub>)<sub>2</sub>·COCl.—This was obtained by the action of phosphorus trichloride on di-isobutylacetic acid. The acid (9 grams) and the phosphorus trichloride (4 grams) were heated together for 10 minutes in an oil bath, the liquid was then decanted from the phosphorous acid, and distilled under reduced pressure. Di-isobutylacetyl chloride is a colourless, pungent-smelling liquid which boils at 95° (20 mm.); it was not analysed, but at once converted into the undermentioned derivatives.

*Di-isobutylacetanilide*, CH(C<sub>4</sub>H<sub>9</sub>)<sub>2</sub>·CO·NH·C<sub>6</sub>H<sub>5</sub>.—This was prepared by dissolving the acid chloride (3 grams) in pure, dry ether, and adding aniline (5 grams) also dissolved in ether. After some time, water was added, the ethereal solution separated and washed with dilute hydrochloric acid until free from aniline, then with water, dried over calcium chloride, and the ether distilled off. The oil which was left slowly solidified, and after being spread on a porous plate to remove oily impurities, was crystallised from light petroleum (b. p. 100—120°). The pure substance was thus obtained in needles melting at 111°. Analysis,

0.1738 gave 9 c.c. nitrogen at 17° and 750 mm. N = 5.92.

CH(C<sub>4</sub>H<sub>9</sub>)<sub>2</sub>·CO·NH·C<sub>6</sub>H<sub>5</sub> requires 5.66 per cent.

Di-isobutylacetanilide dissolves in benzene, alcohol and hot light



petroleum (b. p. 100—120°), but is only sparingly soluble in cold light petroleum.

*Di-isobutylacetoparatoluidide*,  $\text{CH}(\text{C}_4\text{H}_9)_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_3$ , was prepared from the acid chloride and paratoluidine in precisely the same manner as the anilide; it crystallises from light petroleum (b. p. 100—120°) in prismatic needles, melts at 140—141°, and is sparingly soluble in cold light petroleum, but readily in alcohol, chloroform, and benzene.

0.2661 gave 12.6 c.c. nitrogen at 17° and 746 mm.  $\text{N} = 5.36$ .

$\text{CH}(\text{C}_4\text{H}_9)_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_3$  requires  $\text{N} = 5.36$  per cent.

*Di-isobutylacetamide*,  $\text{CH}(\text{C}_4\text{H}_9)_2 \cdot \text{CO} \cdot \text{NH}_2$ , was prepared by adding the acid chloride (3 grams) to concentrated aqueous ammonia (10 c.c.), allowing the mixture to stand for some time, and then extracting with ether; the ethereal solution, dried over potassium carbonate and evaporated, left an oil which slowly solidified. This was purified by crystallising it, first from petroleum boiling at 40—60°, and afterwards from petroleum of high boiling point (100—120°) mixed with a little alcohol, when it was obtained in minute needles melting at 120—121°.

0.1472 gave 10.8 c.c. N at 17° and 750 mm.  $\text{N} = 8.40$ .

$\text{CH}(\text{C}_4\text{H}_9)_2 \cdot \text{CO} \cdot \text{NH}_2$  requires  $\text{N} = 8.18$  per cent.

Di-isobutylacetamide is very soluble in alcohol, but almost insoluble in water, and, when pure, almost insoluble in petroleum of high boiling point.

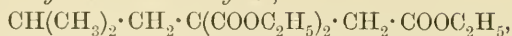
*Preparation of Isobutylsuccinic Acid,*  
 $\text{CH}(\text{CH}_3)_2 \cdot \text{CH}_2 \cdot \text{CH}(\text{COOH}) \cdot \text{CH}_2 \cdot \text{COOH}.$

As this acid was needed for the purpose of comparison with the acid of the formula  $\text{C}_8\text{H}_{14}\text{O}_4$ , which had been obtained by the hydrolysis of ethylic acetylisobutylsuccinate as explained on p. 50, we prepared a considerable quantity of isobutylsuccinic acid by a process which has not been described before. Sodium (2 grams) was dissolved in absolute alcohol (24 grams), mixed with ethylic isobutylmalonate (25 grams), ethylic monochloracetate (14 grams) was added, and the mixture allowed to stand for some hours; it was then heated on the water bath for 4 hours, water was added, and the oil which separated extracted with ether. The ethereal solution, after being well washed with water, dried over calcium chloride and evaporated, left an oil which was purified by fractionation under reduced pressure. In this way a moderately good yield of a substance was obtained which distilled at 170—180° (25 mm.), and, on analysis, gave the following results.

0.1146 gave 0.2484  $\text{CO}_2$  and 0.0886  $\text{H}_2\text{O}$ .  $\text{C} = 59.11$ ;  $\text{H} = 8.58$ .

$\text{C}_{15}\text{H}_{26}\text{O}_6$  requires  $\text{C} = 59.60$ ;  $\text{H} = 8.60$  per cent.

*Ethyl isobutylethanetricarboxylate,*



is a colourless oil which, when distilled under ordinary pressures, appears to undergo but very little decomposition; on hydrolysis, it yields a solid, tribasic acid, which, when heated at  $180^\circ$ , loses carbon dioxide with formation of isobutylsuccinic acid.

The oily ethylic salt was hydrolysed with alcoholic potash in the usual way, the product evaporated until free from alcohol, acidified and repeatedly extracted with ether; after drying over calcium chloride and evaporating, the residual tribasic acid immediately solidified. This was not analysed, but at once converted into isobutylsuccinic acid by heating at  $180$ — $200^\circ$  until carbon dioxide ceased to be evolved; the crude product was then dissolved in hot water, filtered, and saturated with hydrogen chloride; on standing, a mass of crystals separated, which, after two recrystallisations from water, melted at  $109^\circ$ , and consisted of pure isobutylsuccinic acid.

0.1354 gave 0.2764  $\text{CO}_2$  and 0.1002  $\text{H}_2\text{O}$ .  $\text{C} = 55.67$ ;  $\text{H} = 8.22$ .

$\text{C}_8\text{H}_{14}\text{O}_4$  requires  $\text{C} = 55.17$ ;  $\text{H} = 8.04$  per cent.

*Isobutylsuccinanilic acid*,  $\text{C}_4\text{H}_9 \cdot \text{CH}(\text{COOH}) \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_6\text{H}_5$  (?).—In order to prepare this substance, the acid (2 grams) was digested with acetyl chloride for a few minutes, the excess of the latter removed by exposure over potash in a vacuum desiccator, and the residual liquid anhydride dissolved in a little benzene and mixed with aniline (1.5 grams). The solid matter which soon separated, after being drained on a porous plate and recrystallised from dilute alcohol, yielded the anilic acid in beautiful leaflets melting at  $138.5^\circ$ .

0.1818 gave 8.8 c.c. nitrogen at  $15^\circ$  and 558 mm.  $\text{N} = 5.66$ .

$\text{C}_{14}\text{H}_{19}\text{NO}_3$  requires  $\text{N} = 5.62$  per cent.

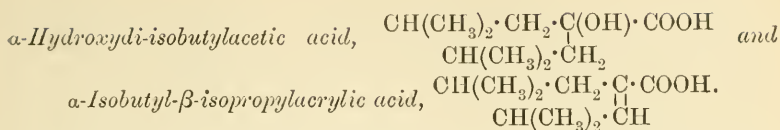
*Isobutylsuccinanil*,  $\text{C}_4\text{H}_9 \cdot \begin{array}{c} \text{CH}-\text{CO} \\ | \\ \text{CH}_2 \cdot \text{CO} \end{array} > \text{N} \cdot \text{C}_6\text{H}_5$ .—This was prepared by

heating the anilic acid at  $200^\circ$  for 5 minutes, and treating the gummy mass obtained with dilute ammonia, when it solidified immediately. This was ground up with dilute ammonia, collected, washed, and recrystallised from dilute alcohol.

0.1352 gave 7.1 c.c. nitrogen at  $16^\circ$  and 752 mm.  $\text{N} = 6.05$ .

$\text{C}_{14}\text{H}_{17}\text{NO}_2$  requires  $\text{N} = 6.06$  per cent.

*Isobutylsuccinanil* melts at  $109^\circ$ , and is readily soluble in alcohol and hot light petroleum, but only sparingly in cold light petroleum; it is almost insoluble in water and in dilute sodium carbonate solution.



In spite of the fact that the boiling point of ethylic acetylisobutylsuccinate (p. 50) is so constant, the numbers obtained on analysis were always nearly 1 per cent. low; this was subsequently found to be due to the fact that it contains traces of bromine. When this ethylic acetylisobutylsuccinate is hydrolysed with hydrochloric acid, there is always a small quantity of oil which remains unattacked, even after the treatment with hydrochloric acid has been repeated several times; in order to ascertain the nature of this oil, the small quantities from several operations were united and fractionated, when nearly the whole passed over at 138—140° (27 mm.), and on examination was found to contain bromine. The analysis of different samples gave the following results.

0.1365	gave	0.2649 CO <sub>2</sub>	and	0.1060 H <sub>2</sub> O.	C = 52.93 ; H = 8.63.
0.1705	„	0.3340 CO <sub>2</sub>	„	0.1320 H <sub>2</sub> O.	C = 53.43 ; H = 8.6.
0.1460	„	0.2880 CO <sub>2</sub>	„	0.1166 H <sub>2</sub> O.	C = 53.80 ; H = 8.87.
0.1214	„	0.2394 CO <sub>2</sub>	„	0.0936 H <sub>2</sub> O.	C = 53.78 ; H = 8.56.
0.2844	„	0.1748 AgBr.		Br = 26.15.	
0.2387	„	0.1502 AgBr.		Br = 26.77.	

These numbers agree with the formula C<sub>13</sub>H<sub>25</sub>BrO<sub>2</sub>, which requires C = 53.2 ; H = 8.5 ; Br = 27.3 per cent.

A careful examination of this oil appears to us to prove that the true formula of the brominated ethylic salt is C<sub>12</sub>H<sub>23</sub>BrO<sub>2</sub>, and that it is, in fact, *ethylic  $\alpha$ -bromodi-isobutylacetate*, C(C<sub>4</sub>H<sub>9</sub>)<sub>2</sub>Br·COOC<sub>2</sub>H<sub>5</sub>. This formula requires C = 51.61 ; H = 8.24 ; Br. = 28.67 per cent., and the discrepancy between these and the numbers actually found was at first thought to be due to the possibility of some of the bromine having been replaced by chlorine during the prolonged boiling with hydrochloric acid. That this is not the case to any appreciable extent is shown by the fact that the 0.1502 gram of silver haloid obtained in one of the above analyses, after being reduced to silver, dissolved in nitric acid, and precipitated with hydrobromic acid, yielded 0.1478 gram of AgBr. Most probably the impurity in the brominated ethylic salt consists of traces of ethylic acetoisobutylsuccinate, which had escaped the hydrolysing action of the hydrochloric acid.

The presence of this brominated substance in the crude ethylic acetoisobutylsuccinate is explained by the fact that when the sodium compound of ethylic malonate is treated with isobutylic bromide, the

principal product is ethylic isobutylmalonate, but there is always formed at the same time some ethylic di-isobutylmalonate,  $C(C_4H_9)_2 \cdot (COOC_2H_5)_2$ .

This ethereal salt, on hydrolysis and subsequent elimination of carbon dioxide, yields di-isobutylacetic acid,  $CH(C_4H_9)_2 \cdot COOH$ , traces of which were evidently present in the isobutylacetic acid used in these experiments. In the subsequent bromination, this would be converted into  $\alpha$ -bromodi-isobutylacetic acid,  $CBr(C_4H_9)_2 \cdot COOH$ , the ethylic salt of which is apparently not readily acted on by the sodium compound of ethylic acetoacetate, since it is found unchanged in the product of the reaction.

*Hydrolysis of Ethylic Di-isobutylbromacetate.*—When the brominated ethylic salt (12 grams) was digested in alcoholic solution with potash (15 grams) in a reflux apparatus, potassium bromide soon began to be deposited in crystals on the side of the flask. After boiling for 8 hours, the product was diluted with water, traces of a neutral oil removed by extraction with ether, and the aqueous solution evaporated with water until quite free from alcohol. The alkaline solution was then acidified, and the oily acid which separated was removed by treatment with ether. The ethereal solution, after drying over calcium chloride and evaporating, left a thick syrup which, on standing for some days over sulphuric acid in a vacuum-desiccator, gradually deposited hair-like crystals; these were collected with the aid of the pump, drained on a porous plate, and then recrystallised from light petroleum.

0.1243 gave 0.2890  $CO_2$  and 0.1206  $H_2O$ .  $C = 63.42$ ;  $H = 10.77$

$OH \cdot C(C_4H_9)_2 \cdot COOH$  requires  $C = 63.88$ ;  $H = 10.64$  per cent.

This beautifully crystalline substance melts at  $123-124^\circ$  and evidently consists of  $\alpha$ -hydroxydi-isobutylacetic acid; it is readily soluble in hot light petroleum (b. p.  $60-80^\circ$ ), sparingly so in the cold, and crystallises from this solvent in slender needles which, when dry, resemble cotton wool.

This acid is isomeric with  $\alpha$ -isopropyl- $\beta$ -isobutylhydracrylic acid (m. p.  $120^\circ$ ),  $CH(CH_3)_2 \cdot CH_2 \cdot CH(OH) \cdot CH(COOH) \cdot CH(CH_3)_2$ , which Wohlbrück (*Berichte*, 1887, 20, 2337) and Hantzsch (*Annalen*, 1888, 249, 65) obtained by the action of sodium on ethylic isovalerate.

The oily filtrate from the crude crystals of the  $\alpha$ -hydroxydi-isobutylacetic acid was fractionated under reduced pressure (35 mm.) when nearly the whole distilled constantly at  $153^\circ$ . The very thick, colourless syrup thus obtained gave the following results on analysis.

0.1793 gave 0.4569  $CO_2$  and 0.1725  $H_2O$ .  $C = 69.50$ ;  $H = 10.69$ .

$C_{10}H_{18}O_2$  requires  $C = 70.06$ ;  $H = 10.60$ .

This substance is evidently isopropylisobutylacrylic acid, and the fraction analysed may contain traces of hydroxydi-isobutylacetic acid,

which would account for the results of the above analysis being somewhat too low.

Isobutylisopropylacrylic acid distils without decomposition under the ordinary pressure at 240—241°. It is almost insoluble in water, but dissolves readily in dilute sodium carbonate solution, and this solution of the sodium salt rapidly decolorises permanganate, although, perhaps, not so readily as is usual with unsaturated acids.

Bromine is slowly decolorised by a solution of the acid in chloroform.

*Salts of Isobutylisopropylacrylic Acid.*—The ammonium salt of this acid dissociates on evaporating its solution on a water bath, ammonia being evolved, and the oily acid separating out. The *silver salt*,  $C_{10}H_{17}AgO_2$ , was obtained as a white, caseous precipitate on adding silver nitrate to a solution of the acid in a slight excess of ammonia; after washing well and drying first on a porous plate and then at 100° it was analysed.

0.2658 gave, on ignition, 0.1040 Ag. Ag = 39.12.

0.2555    "    "    "    0.0998 Ag. Ag = 39.06.

$C_{10}H_{17}AgO_2$  requires Ag = 38.99 per cent.

The neutral solution of the ammonium salt shows the following behaviour with reagents.

*Barium chloride*, no precipitate.

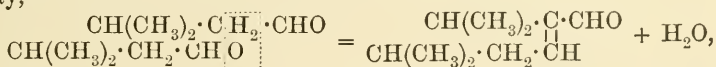
*Calcium chloride.*—If calcium chloride is added to a hot dilute solution of the ammonium salt, a beautifully crystalline characteristic calcium salt rapidly separates; this dissolves in much hot water, but does not appear to crystallise out again on cooling.

*Copper sulphate* gives a very insoluble bluish-green, caseous precipitate.

*Lead acetate*, a white caseous precipitate.

Isopropylisobutylacrylic acid is probably identical with the *amydecylenic acid* which Borodin (*Jahresbericht*, 1870, 680; *Berichte*, 1872, 5, 481) obtained by the oxidation of di-isovaleraldehyde,  $C_{10}H_{18}O$ , a substance which is produced when isovaleraldehyde is digested with potassium carbonate.

If we assume, as is probable, that in the formation of di-isovaleraldehyde two molecules of isovaleraldehyde condense in the following way,



then an aldehyde of this formula should, on oxidation, yield isopropylisobutylacrylic acid and, this appears to be the case, since amydecylenic acid is described by Borodin as an oil boiling at 241.5° without decomposition.

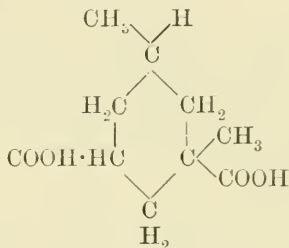


### III.—*Synthesis of an Isomeride of Camphoronic Acid.*

By SAMUEL BARNETT SCHRYVER, Ph.D.

SOME years ago, Wreden (*Ann.*, 1877, 187, 156) showed that when camphoronic acid was heated with concentrated hydriodic acid, it yielded a tetrahydroisoxylene. Again, oxycamphoric acid, when distilled, gives a hydrocarbon isomeric with this and having similar properties, although it is not identical with it, as Aschan, who called it laurene (*Ann.*, 1896, 290, 185), subsequently proved.

These facts, together with others since observed by myself, and which I hope soon to communicate to the Society, led me to the conclusion that camphoric acid was a derivative of metadimethylhexamethylene; and on this assumption the formula for this acid most in agreement with its reaction seemed to be



This constitution would explain the following facts.

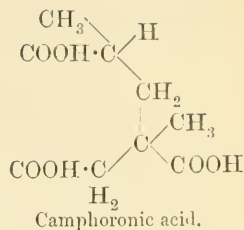
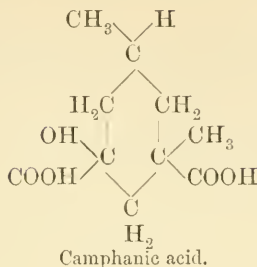
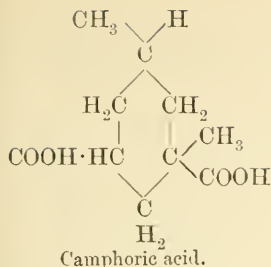
*a.* That when brominated by the action of phosphorus and bromine only a monobromo-derivative is obtainable, for more than one bromine atom has not, as yet, been introduced into the molecule by these means. In accordance with the researches of Hell, Auwers, and others, the bromine always enters in the  $\alpha$ -position relatively to the carboxyl group, and in the above formula only one replaceable hydrogen atom exists in such a position.

*b.* When a hydroxyl group is substituted for the bromine atom, a lactonic acid is produced, hence the bromine atom must be in the  $\gamma$ -position relatively to the second carboxyl group.

Moreover, Reyl er (*Inaug. Dissert. Leipzig*, 1891) has shown that this lactonic acid (camphanic acid), on oxidation, yields camphoronic acid.

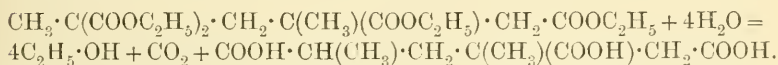
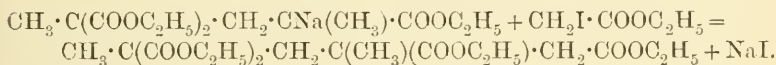
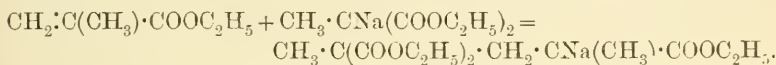
On these assumptions, a formula for camphoronic acid would be derived as follows :





The latter substance was synthesised in the following way.

Ethyl methacrylate was heated with ethyl sodiomethylmalonate according to the method of Auwers, Köbner, and v. Meyenburg (*Ber.*, 1891, **24**, 2887), and the sodio-additive product, without being isolated, was treated directly with ethyl sodacetate and then hydrolysed.



### *Ethyl Methacrylate.*

Ethyl methacrylate is most conveniently prepared by a modification of Frankland and Duppa's method (*Ann.*, 1865, **136**, 12), namely, by the action of phosphorus trichloride on ethyl hydroxyisobutyrate.

*Preparation of Ethyl Hydroxyisobutyrate.*—Hydroxyisobutyric acid dissolved in twice its weight of absolute alcohol containing 3 per cent. of hydrogen chloride is left for a couple of days over fused sodium sulphate, and then heated for 2 hours on a water bath. After fractionation, a portion boiling between 145° and 155° was obtained and used for subsequent operations. The yield is about 50 per cent. of the theoretical.

*Preparation of Ethyl Methacrylate.*—To the ethyl hydroxyisobutyrate prepared as above, about twice the theoretical quantity of phosphorus trichloride is added drop by drop; the mixture is then heated gently for a few minutes on a sand bath, using a reflux condenser, until it begins to get turbid owing to the separation of phosphorus; it is then distilled, &c., one fractionation being sufficient to separate the ethyl methacrylate from the phosphorus compounds. In order to remove the last traces of the latter, the distillate is shaken with a dilute

solution of potassium carbonate. It is advisable to avoid frequent fractionation owing to the ease with which the methacrylate polymerises.

*Synthesis of the Isomeride of Camphoronic acid.*

For this purpose, the ethylic methacrylate is treated with ethylic sodiomethylmalonate, according to the method employed by Auwers and others (*loc. cit.*) in the preparation of dimethylglutaric acid. Instead of decomposing the sodium additive product, however, ethylic iodacetate is added directly to the alcoholic solution; the mixture becomes hot, and the reaction is completed by heating it in a corked soda water bottle at  $100^{\circ}$  until it is nearly neutral. The alcohol is then distilled off, and the oily residue washed with water. As the molecular weight of the ethylic salt thus obtained is so high that it cannot be advantageously submitted to fractional distillation, it is hydrolysed directly with twice its volume of hydrochloric acid (1 water : 1 acid), as recommended by Auwers in similar cases.

The product, after being filtered and distilled with steam, to separate the propionic and other volatile acids formed, is extracted several times with ether. It is advisable to put a little animal charcoal into the flask during the steam distillation, so as to decolorise the liquid. The ethereal extract contains much methylsuccinic acid formed by the action of the ethylic iodacetate on unchanged ethylic methylmalonate; there is, however, another acid present, which can be separated from the rest owing to the fact that, *like camphoronic acid, it forms a lead salt insoluble in acetic acid*. Accordingly, the residue left on evaporating the ethereal extract is dissolved in water, and lead acetate is added *without previously neutralising the solution*; the precipitate of lead salt, after being washed with water, alcohol, and ether, is dried, suspended in ether, and decomposed by dry hydrogen sulphide. On evaporating the filtrate from the lead sulphide, an almost colourless syrup is left, which does not crystallise even after standing for several months in a desiccator.

Attempts were made to prepare a crystalline anhydride from it on the assumption that the syrup was a mixture of geometrical isomerides and therefore not easily crystallisable. For this purpose, it was treated with acetyl chloride, when a minute quantity of crystals separated; water was then added to the acetyl chloride solution, the acetic acid removed by evaporation, and a silver salt prepared by precipitation. This, after being washed and dried, was suspended in ether and decomposed by hydrogen sulphide, but on evaporating the ether a syrup was again obtained. This was dissolved in strong nitric acid, when a slight oxidation took place, and the solution was immediately diluted with an equal bulk of water. After some time, crystals

of the hydroxy-acid began to separate in hard, indistinct crusts, and these, after being separated from the mother liquor, and dried over sulphuric acid and caustic soda in a vacuum, so as to free them from the last traces of water and nitric acid, were recrystallised once or twice from ether which had been distilled over sodium. The substance was thus obtained in snow white, microscopic crystals melting sharply at 137°.

0.1448 gave 0.2452 CO<sub>2</sub> and 0.794 H<sub>2</sub>O. C = 46.18; H = 6.09.

C<sub>9</sub>H<sub>14</sub>O<sub>7</sub> requires C = 46.15; H = 5.98 per cent.

It may be remarked that camphoronic acid, when treated with nitrohydrochloric acid, is also oxidised to oxycamphoronic acid.

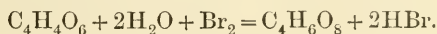
It had been my intention to prepare this acid in larger quantities and investigate its salts, but the synthesis takes a long time to carry out and is costly. As, moreover, Drs. W. H. Perkin, jun., and J. T. Thorpe published their synthesis of the true camphoronic acid at the time my work had reached the stage described, the main object with which it had been undertaken was accomplished, and I have therefore been compelled to relinquish any further investigations in this direction.

#### IV.—*Properties and Relationships of Dihydroxytartaric Acid. Part I.*

By HENRY J. HORSTMAN FENTON, M.A.

THIS acid was first observed by Grüber, who obtained it, in solution, by the action of nitrous acid on protocatechuic acid (*Ber.*, 1879, 12, 514). It was afterwards prepared from pyrocatechol by Barth (*Sitz. Acad. Wein*, 82, ii, 1024); from guaiacol by Werzig, and from "nitrotartaric acid" by Kekulé (*Annalen*, 1883, 221, 230) in a similar manner; these authors isolated it in the form of the sparingly soluble sodium salt, and from this the free acid was subsequently obtained by Miller (*Ber.*, 1889, 22, 2015). The salt was decomposed by hydrogen chloride under ether, excess of hydrogen chloride being avoided and moisture carefully excluded; but since its isolation by Miller, the free acid appears to have been scarcely examined.

In a former communication (*Trans.*, 1895, 67, 48), it was shown that a solution of dihydroxytartaric acid may very easily be obtained by the oxidation of the new acid C<sub>4</sub>H<sub>4</sub>O<sub>6</sub> (dihydroxymaleic acid) with bromine in presence of water. The change takes place nearly quantitatively according to the equation



The solution was precipitated with sodium carbonate, and the free acid prepared from the sodium salt by Miller's method. The yield of free acid obtained by this method appears to be small, probably owing to its very sparing solubility in anhydrous ether. It was mentioned, however, that the free acid might be directly obtained from the solution after oxidation with bromine, without first preparing the sodium salt; this was effected by concentrating the solution in a vacuum desiccator over solid potash, but the purity of the product was uncertain. Further experiments have now shown that, by modifying the details previously given, this process affords a very simple and productive method for the preparation of the acid in a state of purity.

Having regard to the very interesting constitution of this acid and to the close relation which has been shown to exist between it and dihydroxymaleic acid, it was considered desirable to take advantage of this new method of preparation and to make a study of the properties of the acid.

#### *Preparation of the Acid.*

Crystallised dihydroxymaleic acid,  $C_4H_4O_6 \cdot 2H_2O$ ,\* is well triturated with from 4 to 5 times its weight of glacial acetic acid; and rather more than the calculated quantity of bromine, dissolved in a little glacial acetic acid, is added to the mixture in small portions at a time. The first portions are almost instantly bleached, but the action afterwards becomes more sluggish and apparently ceases—a few drops of water are then added, whereupon the colour of the bromine is again immediately discharged. The addition of bromine is continued until the colour is quite permanent on standing, even when a drop or two of water is added. It has been previously shown (*loc. cit.*) that this final stage is reached when the bromine has been added in about the calculated proportion (1 mol. acid to 1 mol. bromine); fumes of hydrogen bromide are freely evolved during the operation. The dihydroxymaleic acid is nearly insoluble in cold glacial acetic acid, but when the oxidation is finished complete solution takes place. The solution is allowed to stand for an hour or two, and then vigorously stirred, when the dihydroxytartaric acid quickly, sometimes suddenly, separates as a heavy, white, crystalline powder.

The product is now collected and drained with the aid of the pump, washed once or twice with small quantities of anhydrous ether, and kept in a vacuum desiccator over solid potash and sulphuric acid to remove the last traces of hydrobromic acid, acetic acid, bromine and ether. The yield of purified product thus obtained is 70 per cent. or more of the theoretical. Thus, using 18.4 grams of dihydroxy-

\* For the preparation of this acid, see Trans., 1894, 65, 901.

maleic acid, 80 c.c. of acetic acid, and 5.5 c.c. of bromine, the yield of pure product was 13.3 grams. Theory = 18.2 grams. Again, with 28 grams of dihydroxymaleic acid, 120 c.c. of acetic acid, and 9 c.c. of bromine, the yield was 21 grams. Theory = 27.7 grams. The remainder may of course be recovered as sodium salt by neutralising with sodium carbonate.

The product thus obtained, when heated in a capillary tube, melts sharply, and decomposes, at 114—115°. The acid previously prepared by Miller's method melted and decomposed at 98°.

I. 0.1492 gave 0.1421  $\text{CO}_2$  and 0.0443  $\text{H}_2\text{O}$ . C = 25.97; H = 3.29.

II. 0.1736 „ 0.1667  $\text{CO}_2$  „ 0.0516  $\text{H}_2\text{O}$ . C = 26.18; H = 3.30.

$\text{C}_4\text{H}_6\text{O}_8$  requires C = 26.37; H = 3.30 per cent.

### *Action of Heat.*

#### *Preparation of Tartronic Acid.*

*Dry Acid.*—It might perhaps be expected from the constitution of dihydroxytartaric acid that it would tend to lose water on heating, giving the diketonic acid,  $\begin{array}{c} \text{CO}\cdot\text{COOH} \\ | \\ \text{CO}\cdot\text{COOH} \end{array}$ , especially as Anschütz has shown (*Annalen*, 1891, 261, 130) that the ethylic salt has a composition corresponding to this acid; it is found, however, that the free acid when heated at 90° in a current of dry hydrogen for about one hour, undergoes no loss in weight. Heated in a vacuum on a water bath at 90—100°, it loses weight slowly and somewhat irregularly, and gradually turns dark brown without melting; the loss of weight after 5 hours heating was about 42 per cent., that is, considerably more than is represented by the loss of all the hydrogen as water. The residue, moreover, when dissolved in water and tested with sodium carbonate, no longer gives the reaction of dihydroxytartaric acid.

*Aqueous Solution.*—Grüber showed that the sodium salt, when heated with water, is resolved into sodium tartronate and carbon dioxide. An aqueous solution of the free acid is found to undergo a similar change; when this is gently heated, carbon dioxide is freely evolved, and the solution, after concentration, yields crystals of pure tartronic acid, as will be seen from the following results.

A few grams of dihydroxytartaric acid were dissolved in water, the solution heated on a water bath until carbon dioxide ceased to be evolved, and then concentrated to a small bulk and allowed to stand in a desiccator; in a few days, long, transparent prisms separated, which, after being drained on filter paper, air dried, and then heated at 100° until the weight was constant, were analysed.

I. 0.1603 gave 0.1750  $\text{CO}_2$  and 0.0476  $\text{H}_2\text{O}$ . C = 29.76; H = 3.29.

Tartronic acid,  $\text{C}_3\text{H}_4\text{O}_5$  requires C = 30.00; H = 3.33 per cent.



11. 0.6067 substance, on titration, required 12.4 c.c. of a solution of caustic soda containing 0.0187 Na per c.c. Theory for a dibasic acid,  $C_3H_4O_5 = 12.0$  c.c.

The crystals melted at 158—159°; the melting point of tartronic acid has been very variously given by different authors, but Grüber (*loc. cit.*), and Massol (*Compt. rend.*, 1892, 114, 422), both obtained anhydrous crystals melting at 155°.

[The crystals appear to separate from the solution in the anhydrous state, and not with  $\frac{1}{2}H_2O$  as sometimes stated, since they undergo scarcely any change in appearance when heated at 100°. The *air dried* crystals gave, on analysis,

C = 29.14 ; H = 3.27.  $C_3H_4O_5, \frac{1}{2}H_2O$  would require C = 27.9 ; H = 3.8.

The water is, therefore, probably only "mechanical."]

This reaction, then, affords an extremely easy and productive method for the preparation of pure tartronic acid; the yield is almost theoretical, and the product is pure without recrystallisation. Thus 0.9696 gram of dihydroxytartaric acid was dissolved in water, the solution heated as described above, taking care to avoid loss by spirting, and then allowed to evaporate in a vacuum desiccator; the crystalline residue dried at 100° until the weight was constant, melted at 157—158°, and its weight was 0.6237 gram, theory requiring 0.6392 gram.

#### *Titration by Alkalis.*

Judging from the observation, above referred to, that sodium dihydroxytartrate, when heated, decomposes into sodium tartronate and carbon dioxide, Grüber considered that the acid was "carboxytartronic" acid,  $\begin{matrix} \text{COOH} \\ \text{COOH} \end{matrix} > \text{C}(\text{OH}) \cdot \text{COOH}$ , and consequently that the sodium compound was an *acid* salt. Attempts to prepare the normal salt were, however, unsuccessful. Grüber found that the sodium salt was not acted on by a dilute solution of caustic soda, and Barth showed that dry ammonia was also without action on it; a strong solution of caustic soda dissolves it, but apparently decomposes it, since the sparingly soluble salt cannot be again obtained from the solution after acidification. Barth, however, prepared and analysed the barium salt and found its composition to be  $\text{Ba}_3(\text{C}_4\text{HO}_7)_2, 3\text{H}_2\text{O}$ , corresponding with the normal salt of a tribasic acid  $\text{C}_4\text{H}_4\text{O}_7$ .

Since this acid had been obtained from benzenoid compounds and was regarded as tribasic, with one carbon atom directly associated to three others, arguments were advanced from its supposed constitution which were at variance with Kekulé's well known benzenesymbol. Kekulé then made an exhaustive study of the sodium salt obtained from various sources. He showed also that it could be prepared from

“nitrotartaric” acid, and that by reduction with zinc and acid, modifications of tartaric acid were produced. His results indicated that the acid is in reality *dibasic*, having the formula  $C_4H_6O_6$  (dihydroxytartaric acid, or tetrahydroxysuccinic acid), and that the sodium compound is a *normal* salt; he suggests that the barium salt obtained by Barth, if it is a homogeneous substance, may be a basic salt, or that replacement may have taken place in the hydroxyl groups.

The acid being now available in quantity, and in a pure state, it was considered that the results of titration by various alkalis might be of interest, as affording further evidence with regard to the basicity of the acid. Experiments were accordingly made, using sodium, potassium, and barium hydroxides, as well as ammonia and sodium carbonate, with the following results.

I. 0.3778 gram of acid dissolved in 5 c.c. of water required 6.9 c.c. of a solution of caustic soda, prepared from metallic sodium, containing 0.01877 Na per c.c.; phenolphthalein was used as indicator, and the most minute precautions were taken in order to ensure the exclusion of carbon dioxide, not only during the preparation of the solution, but also from the water employed, and during the operation of titration.

One mol. of acid required, therefore, 2.7 mols. NaOH for neutralisation.

II. 0.6035 gram of acid in 5 c.c. of water required 8.7 c.c. of normal KOH solution. (Phenolphthalein as indicator.) One mol. of acid neutralised 2.6 mols. of KOH.

III. 0.6035 gram of acid in 5 c.c. of water required 6.4 c.c. of normal sodium carbonate. (Methyl-orange as indicator.) One mol. of acid neutralised 0.96 mol. of  $Na_2CO_3$ .

IV. 0.2910 gram of acid required 15.5 c.c. of barium hydroxide solution containing 0.0225 gram of  $Ba(OH)_2$  per c.c. (Phenolphthalein as indicator.) One mol. of acid neutralised 1.27 mols. of  $Ba(OH)_2$ .

V. 0.4218 gram of acid in about 10 c.c. of water required 11.3 c.c. of a solution of pure ammonia containing 7.5555 gram  $NH_3$  per litre. (Litmus as indicator.) One mol. of acid neutralised 2.16 mols. of  $NH_3$ .

The colour indications with phenolphthalein, although sharp at first, quickly faded, and another drop or so of alkali was required to restore the colour; in the case of litmus, the blue colour quickly changed to wine-red in a similar way. The numbers given represent the amount of alkali required to give a colour change which was permanent for a few minutes; the differences between the initial and final colour-change, however, were small, amounting only to about 0.2 to 0.3 c.c.

These results would appear to indicate that dihydroxytartaric acid behaves normally as a dibasic acid towards sodium carbonate and

ammonia, but that with the hydroxides of sodium, potassium, and barium, its behaviour is intermediate between that of a dibasic and a tribasic acid.

At first it seemed probable that the high results obtained when "strong" bases are employed might be explained by supposing that one or more of the alcoholic hydroxyl groups in the acid exerted "acid" functions and that the compounds formed are more or less hydrolysed; or that the acid might in reality be tribasic carboxy-tartronic acid as was formerly believed, the replacement of the third atom of hydrogen giving rise to an unstable salt as in the case of orthophosphoric acid.

Dilution of the solution, however, has but little effect, as seen by the following experiments.

VI. 0.3158 gram of acid dissolved in 50 c.c. of water required 5.45 c.c. of NaOH solution containing 0.0189 gram Na per c.c. One mol. of acid neutralised 2.6 mols. of NaOH.

VII. 0.3391 gram of acid dissolved in 150 c.c. of water required 5.8 c.c. of the same NaOH solution. One mol. of acid neutralised 2.5 mols. of NaOH.

The high results might, on the other hand, be due to the partial decomposition, at the ordinary temperature, of the acid into dibasic tartronic acid and carbon dioxide; such a decomposition would not influence the result when methyl-orange was used as indicator, but would give a high result with phenolphthalein. Various experiments were therefore made in order to throw light upon this question.

VIII.—A standard solution of the acid was prepared and a portion titrated immediately with soda; the remainder of the solution was allowed to stand for about 2 hours and an equal portion again titrated with the same soda. The two results were practically identical.

IX.—Air, carefully purified from carbon dioxide by passing it through strong caustic soda solution and then through baryta-water, was allowed to bubble through a freshly prepared solution of 0.3208 gram of acid in about 10 c.c. of water contained in a small flask. The issuing gas was carefully tested for carbon dioxide by passing it through a series of bulbs containing baryta water; no trace of turbidity could be detected for the first 10 or 12 minutes, after which, however, a faint cloudiness was perceptible in the first bulb.

From the results of these last two experiments it appears to be very improbable that the high results on titration can be due to the decomposition of the acid itself. But it may be that the *salt* produced is less stable than the acid, and breaks up in the manner indicated.

X.—0.3223 gram of acid was dissolved in about 10 c.c. of water and the experiment conducted exactly as in IX, but with the alteration that, as soon as the acid had dissolved, standard caustic soda was run in

from a burette in quantity insufficient for neutralisation (about 0.054 gram Na). Carbon dioxide was, in this case, given off almost immediately; after 3 minutes there was a dense turbidity in the first baryta bulb and after 5 minutes all three bulbs were turbid. The soda solution had been prepared from metallic sodium with great precautions to exclude carbon dioxide, and the apparatus from which it was supplied was constructed so as to avoid the possibility of contamination. Still it was considered advisable to make a blank test with the whole apparatus, and this was done, dilute sulphuric acid being partially neutralised with the same soda solution and the experiment conducted exactly as before. No trace of carbon dioxide could be detected after passing the air for 10 minutes.

It is tolerably certain therefore that the high results on titration are due to the splitting up of the salts produced into tartronate and carbon dioxide; if this is so, one would expect that lower, if not normal, results should be obtained on cooling the solutions, the titrations mentioned all having been performed at the ordinary temperature of the laboratory. This indeed, is found to be the case.

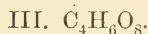
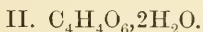
XI.—0.4498 gram of acid in about 10 c.c. of water was cooled by ice and standard caustic soda containing 0.02183 gram of Na per c.c. was slowly run in, phenolphthalein being used as indicator. 5.4 c.c. were required for neutralisation. One mol. of acid neutralised 2.07 mols. of NaOH.

XII.—0.3201 gram of acid in about 10 c.c. of water was cooled, as above, and titrated with pure ammonia solution containing 7.5555 grams of  $\text{NH}_3$  per litre; 7.9 c.c. were required. Litmus was used as indicator and the final blue colour was permanent for 5 minutes or more. One mol. of acid neutralised 1.99 mols. of  $\text{NH}_3$ .

XIII.—0.3076 gram of acid in about 10 c.c. of water, cooled as before, required 14.7 c.c. of baryta water containing 0.02244 gram of  $\text{Ba}(\text{OH})_2$  per c.c. (phenolphthalein as indicator). One mol. of acid neutralised 1.14 mols. of  $\text{Ba}(\text{OH})_2$ .

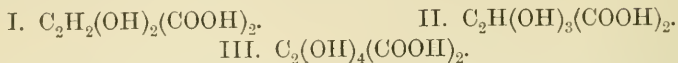
*Reduction of Dihydroxytartaric Acid to the Acid  $\text{C}_4\text{H}_4\text{O}_6$ .*

It has already been pointed out (Trans., 1895, 67, 48) that the new acid,  $\text{C}_4\text{H}_4\text{O}_6$  (dihydroxymaleic acid and its isomeride), may be regarded as intermediate between tartaric and dihydroxytartaric acids; that is, the anhydrous acid contains 2 atoms of hydrogen *less* than tartaric acid, and the hydrated acid contains two atoms of hydrogen *more* than dihydroxytartaric acid



Or, if it be assumed, as is not improbable (*loc. cit.*, 67, 777), that a

solution of the acid  $C_4H_4O_6$  contains trihydroxysuccinic acid, the relation is perhaps better illustrated thus,



The conversion of I into II is brought about by the oxidation of tartaric acid in presence of ferrous iron, of II into I by hydrogen iodide, and II is easily oxidised to III by bromine and water.

The missing transformation was that of III into II, that is, the reduction of dihydroxytartaric acid to the acid  $C_4H_4O_6$ . This transformation has now been effected in several ways, and can be very easily recognised owing to the striking difference in properties between the two acids; for example, dihydroxytartaric acid is very easily soluble in cold water, deliquesces slowly on exposure to the air, and its aqueous solution gives no colour reaction with ferric chloride. On the other hand, both the  $\alpha$  and  $\beta$  forms of the acid  $C_4H_4O_6$  are very sparingly soluble in cold water, and the hydrated crystals,  $C_4H_4O_6 \cdot 2H_2O$ , are quite permanent in the air; moreover, their aqueous solutions give a transient, emerald-green coloration with ferric chloride in presence of mineral acids, and a beautiful blue-violet with ferric chloride followed by caustic alkali in excess.

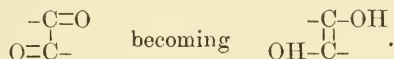
*Action of Zinc and Dilute Acid.*—Kekulé (*loc. cit.*, 239) showed that sodium dihydroxytartrate, when treated with excess of zinc and hydrochloric acid, gave rise to racemic and inactive tartaric acids (together with a small quantity of a substance assumed to be tartronic acid). This change is usually explained by supposing the dihydroxytartaric acid to behave as a diketonic acid,  $\begin{array}{c} CO \cdot COOH \\ | \\ CO \cdot COOH \end{array}$ .

It is now found that, by using a limited quantity of zinc, the acid  $C_4H_4O_6$  may be isolated as an intermediate stage. To dihydroxytartaric acid (1 mol.) dissolved in water, and mixed with granulated zinc (1 atom), dilute sulphuric acid was gradually added, the mixture being kept cold by ice; when all the zinc had dissolved, a portion of the liquid, on being tested with ferric chloride, was found to give strongly marked colour reactions characteristic of the acid  $C_4H_4O_6$ . The remainder of the liquid was carefully mixed with about one-tenth of its volume of strong sulphuric acid, twice extracted with ether, and the ethereal solution evaporated; the white residue thus obtained was very sparingly soluble in cold water, but dissolved readily in warm water, and the aqueous solution showed all the reactions of the acid  $C_4H_4O_6$ . On cooling this solution, crystals separated which, when examined under the microscope, were found to consist *entirely* of the  $\beta$ -modification of the acid.\*

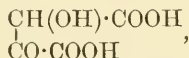
\* Commercial sodium dihydroxytartrate gave an exactly similar result.



The constitution of this  $\beta$ -modification has not yet been ascertained, but it was shown (*loc. cit.*, 69, 561) that, not improbably, it is dihydroxyfumaric acid. If so, its production in the manner just described would seem to be somewhat analogous to the formation of pinacones, the group



But this  $\beta$ -acid may, instead, have the alternative formula suggested, namely,



in which case the change would be readily understood.

*Hydrogen sulphide* or *stannous chloride*, when used in limited quantity, effects a similar reduction.

*Action of Hydrogen Bromide.*—Attempts were made by various methods to bring about the dehydration of dihydroxytartaric acid, and, with this object in view, the action of hydrogen bromide was studied. It has been previously shown that, in the case of dihydroxymaleic acid, the action of hydrogen bromide in glacial acetic acid solution brings about, as a final effect, the loss of 1 mol.  $\text{H}_2\text{O}$  with production of the substance  $\text{C}_4\text{H}_2\text{O}_5$  (which appears to be the lactonic acid corresponding with the  $\beta$ -form of the acid).

Dihydroxytartaric acid, however, when submitted to this treatment, gave an altogether unexpected result. About 25 grams of the acid were mixed with 250 c.c. of glacial acetic acid, and the mixture saturated with dry hydrogen bromide at about  $15^\circ$ , when the acid dissolved completely after standing and shaking. The solution, after about 2 days, was heated in a pressure-bottle at  $60\text{--}70^\circ$  for 2 hours, and the product, which was bright orange-red, was then distilled down to a small bulk under reduced pressure. It was observed that practically all the colour passed over with the first half, or so, of the distillate, leaving a colourless residue in the distilling flask. This residue, which set to a crystalline mass on cooling, was found to consist of two substances, one of which was very easily soluble in ether, glacial acetic acid, or cold water, whilst the other was very sparingly soluble in these solvents; the appearance of the product was exactly like that which had been obtained in the case of *dihydroxymaleic acid*, and on testing it with ferric chloride and alkali, both the easily and the sparingly soluble portions were found to give the reactions of *that acid*.

The sparingly soluble substance was then dissolved in the smallest possible quantity of hot water and cooled as quickly as possible, to avoid loss by decomposition, which began on heating, when crystals began to separate almost immediately; these, on examination under the microscope, were seen to consist of the characteristic diamond-

shaped plates of dihydroxymaleic acid. A few crystals of the  $\beta$ -acid could also be distinguished, but this, of course, might be expected since the  $\alpha$ -form is slowly transformed into the  $\beta$ -form by hydrogen bromide. The crystals were collected, washed with a small quantity of cold water, air dried on filter paper for 24 hours, and analysed.

0.1538 gave 0.1459  $\text{CO}_2$  and 0.0577  $\text{H}_2\text{O}$ .  $\text{C} = 25.87$ ;  $\text{H} = 4.16$ .

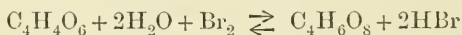
$\text{C}_4\text{H}_4\text{O}_6, 2\text{H}_2\text{O}$  requires  $\text{C} = 26.08$ ;  $\text{H} = 4.02$  per cent.

That part of the residue which dissolved easily in ether, &c., corresponded exactly with the product obtained when dihydroxymaleic acid was acted on by hydrogen bromide in acetic acid solution; the ethereal solution, on evaporation, gave radiating, feathery crystals which were extremely deliquescent. It dissolved in alkalis giving a bright lemon-yellow solution, and on adding ferric chloride, the characteristic blue-violet coloration was produced. The aqueous solution, on standing for some hours, gave short prisms of the  $\beta$ -acid.

It follows, therefore, from these results, that when *dihydroxytartaric* acid is acted on by excess of hydrogen bromide in presence of acetic acid, and the mixture afterwards distilled, a crystalline product is left which is identical with that obtained when *dihydroxymaleic* acid is treated in the same manner. The liquid distillate, however, is quite different. In the case of dihydroxymaleic acid, it is practically colourless and consists only of acetic and hydrobromic acids; but with dihydroxytartaric acid the first portions of the distillate are bright orange-red. When this distillate is diluted with water and shaken with ether or with carbon bisulphide, the orange-red substance may be extracted, and is found, by all the usual tests, to be bromine.

Dihydroxytartaric acid therefore acts as an oxidising agent towards hydrogen bromide, liberating bromine, and becoming itself reduced to the acid  $\text{C}_4\text{H}_4\text{O}_6$ .

This is the converse of the change by which dihydroxytartaric acid was prepared in the manner described above. The reaction



is therefore a reversible one, the direction depending on the masses of the reacting substances, and probably to some extent on the temperature. The forward \* change is brought about at the ordinary temperature, when bromine is added in excess, some water introduced, and the operation conducted in an open dish so as to allow of the free escape of hydrogen bromide. The reverse change takes place when a large excess of hydrogen bromide is used, and the mixture is heated in a closed vessel and afterwards distilled; it can take place, to some

\* The terms "forward" and "reverse" are used, for shortness ' in the sense indicated by the arrows.

extent at any rate, at the ordinary temperature, for if dihydroxy-tartaric acid is mixed with excess of a saturated solution of hydrogen bromide in glacial acetic acid, allowed to stand a few hours, and then kept in a vacuum desiccator over solid potash and sulphuric acid, the residue gives strongly marked reactions of dihydroxymaleic acid as well as of those of dihydroxytartaric acid. If the orange-yellow solution, referred to above, be treated with water, it is instantly bleached, whereas the orange-yellow distillate obtained from it is not affected by water.

It is possible that, both in the forward and reverse changes, the unstable compound,  $C_2(OH)_2Br_2(COOH)_2$  (dibromotartaric acid), is first produced as an intermediate stage, and that this, by the action of water, gives dihydroxytartaric acid, or by loss of bromine gives dihydroxymaleic acid.

The reversibility of this action explains the fact, above mentioned, that, on adding bromine to the crystallised acid, the action appears to cease considerably before the calculated quantity of bromine has been introduced, but again proceeds rapidly on the addition of a small quantity of water.

## V.—Stereochemistry of Unsaturated Carbon Compounds. Part I. Etherification of Substituted Acrylic Acids.

By JOHN J. SUDBOROUGH and LORENZO L. LLOYD.

IN a series of communications presented to the German Chemical Society (*Ber.*, 1894, 27, 510, 1580, and 3146), Victor Meyer and one of us were enabled to show that, as regards the ease with which they are etherified, diortho-substituted benzoic acids differ completely from

their isomerides. Acids of the type  $\begin{array}{c} \text{COOH} \\ \diagup \quad \diagdown \\ \text{X} \quad \quad \text{X} \end{array}$ , where  $\text{X} = \text{Cl}, \text{Br}, \text{NO}_2$ ,

$\text{COOH}$ , &c., are entirely unacted on when their methyl alcoholic solutions are saturated with dry hydrogen chloride, either in the cold or at the boiling point of the alcohol. Acids in which  $\text{X} = \text{CH}_3, \text{OH}, \text{F}$ , &c., that is in which the weights of the substituting groups are small, yield minute quantities of their methylic salts when their boiling solutions are treated with hydrogen chloride for some time (V. Meyer, *Ber.*, 1895, 28, 1259). V. Meyer has since shown that the method of etherification suggested by E. Fischer and Speier (*Ber.*, 1895, 28, 3252), in

which the acid is boiled with a 3 per cent. solution of hydrogen chloride, yields similar results, and is preferable to the method first adopted, as many acids, which are but sparingly soluble or practically insoluble in cold methylic alcohol, dissolve readily on warming. It was stated by Victor Meyer and one of us that this abnormal behaviour of diortho-substituted benzoic acids is to be attributed to stereochemical causes, and Wegscheider (*Monatsh.*, 1895, 16, 75) has since suggested that, if etherification be preceded by the formation of an additive compound of the acid and alcohol, the groups or atoms in the ortho-positions may be in such proximity to the carboxylic group as to hinder or completely prevent the formation of the additive compound. This view is supported by the fact that the radical weight or volume plays an important part in the retardation or prevention of etherification (Meyer, *Ber.*, 1895, 28, 1259). Recent investigations by Kellas (*Zeit. phys. Chem.*, 1897, 24, 221) prove that the retardation is not merely due to the weight of the group in the ortho-position, as among ortho-substituted benzoic acids the nitro-group ( $\text{NO}_2 = 46$ ) has a greater retarding influence than either bromine or iodine ( $\text{Br} = 80$ ,  $\text{I} = 127$ ).

Menschutkin has also been able to draw generalisations regarding the etherification of saturated acids of the aliphatic series from his researches on primary, secondary, and tertiary fatty acids \* (*Annalen*, 1879, 195, 334, and 1879, 197, 193).

Formic acid.....	61.7 p. cent.	Isobutyric acid .....	29.0 p. cent.
Acetic acid .....	44.4 „	Methylacetic acid .....	21.5 „
Propionic acid...	41.2 „	Trimethylacetic acid .....	8.3 „
Butyric acid ...	33.3 „	Dimethylethylacetic acid	3.5 „

From these results, it is evident that an acid with the grouping  $\begin{smallmatrix} \text{R} \\ \text{R}_I \end{smallmatrix} \begin{array}{c} \diagup \\ \diagdown \end{array} \text{C} \cdot \text{COOH}$  is much more difficult to convert into its ethereal salt than acids of the types  $\text{RCH}_2 \cdot \text{COOH}$  and  $\text{RR}_I\text{CH} \cdot \text{COOH}$ , where R,  $\text{R}_I$ , and  $\text{R}_{II}$  represent alkyl groups. The broader generalisation, that

acids of the type  $\begin{smallmatrix} \text{X} \\ \text{X}_I \\ \text{X}_{II} \end{smallmatrix} \begin{array}{c} \diagup \\ \diagdown \end{array} \text{C} \cdot \text{COOH}$ , where X not only represents alkyl groups but also Cl, Br,  $\text{NO}_2$ , &c., are difficult to etherify, does not, however, hold good, since trichloroacetic acid is more readily etherified than acetic acid itself. A reason for this anomalous behaviour of trihalogenised acetic acid has been put forward by Feilmann and one of us (*Proc.*, 1897, 241).

\* These numbers represent the initial velocity or the amount of acid (in percentage of the quantity originally present) converted into ethereal salt when molecular quantities of the acid and isobutylic alcohol are heated at  $155^\circ$  for 1 hour.

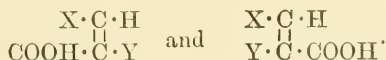
Although generalisations of the above nature have been made with reference to substituted benzoic acids, and also to the fatty acids, no systematic study of unsaturated acids appears to have been made; we therefore determined to prepare a number of the latter and to study the amounts of ethereal salt formed under different conditions, in order to find whether any general rules could be drawn from the results. A further incentive to this study was the suggestion made by one of us (*Chem. News*, 1895, 72, 187) with reference to the constitution of camphoric acid. In that note, attention was drawn to the fact that Bredt's constitutional formula accounts for the characteristic behaviour of camphoric acid on etherification with ethylic alcohol and hydrogen chloride, if the assumption be made that an acid with the grouping



is difficult to etherify. At the time this suggestion was put forward, no facts were known which justified the assumption, and it was partly with the object of determining whether further investigations might supply satisfactory evidence on this point that the present research was started. Acids of the type mentioned are by no means common, whereas many acids are known of somewhat similar constitution, namely, unsaturated acids of the type



We selected the latter class of acids as being the most suitable, and also because it seemed interesting to determine whether there was any great difference in the amounts of ethereal salt formed by the stereoisomeric acids



During the course of this investigation, a communication by Anschütz (*Ber.*, 1897, 30, 2652) appeared which bears on the same subject, with the exception that he investigated a few dicarboxylic acids, whereas we have restricted ourselves to the study of monobasic acids. In the summary at the end of this paper, we discuss Anschütz's results and compare them with our own.

The following is a list of the acids we have investigated.

Cinnamic acid, allocinnamic acid, atropic acid, ortho-, meta-, and para-nitrocinnamic acids.

$\alpha$ -Bromocinnamic acid and  $\alpha$ -bromallocinnamic acid.

The two isomeric  $\beta$ -bromocinnamic acids.

The two isomeric  $\alpha\beta$ -dibromocinnamic acids.

Dichloro- and di-iodo-cinnamic acids.



$\alpha$ -Cyanocinnamic acid, orthonitro- $\alpha$ -cyano- and metanitro- $\alpha$ -cyano-cinnamic acid.

$\alpha$ -Phenylcinnamic acid and  $\alpha$ -phenylallocinnamic acid.

$\alpha$ -Phenylorthonitrocinnamic acid,  $\alpha$ -phenylorthonitro-allocinnamic acid and the corresponding meta- and para-compounds.

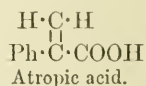
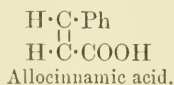
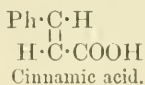
Triphenylacrylic acid.

$\alpha\beta$ -Di-iodoacrylic acid.

The results obtained are given in tabular form at pp. 91—92.

In some of our earlier experiments, we attempted to etherify the acids by saturating their methyl alcoholic solutions with hydrogen chloride in the cold and allowing the mixture to stand for some time, but we found that this method was not adapted to our purpose, as certain acids, especially nitrated acids, were almost insoluble in cold methylic alcohol and, therefore, yielded little or no ethereal salt by this treatment. In all the later experiments, namely, those described in this paper, we used the Fischer-Speier method. A considerable amount of a 3 per cent. solution of hydrogen chloride in pure methylic alcohol (3 grams HCl in 100 grams of solution) was prepared, and half a gram of the acid was boiled with 10 c.c. of this solution for an hour on the water bath, in a small flask fitted with a reflux condenser. For this purpose, the condenser described by Feilmann and one of us (*J. Soc. Chem. Ind.*, 1897, 16, 979) is admirably adapted, as it does away with the possibility of moisture permeating the cork and thus vitiating the result. At the end of the specified time, water was added and the whole extracted twice with ether, any unaltered acid was removed by the aid of dilute sodium carbonate, and the ethereal solution, after drying with calcium chloride, was slowly distilled from a tared flask. The amount of ethereal salt formed was weighed after the flask had been standing over sulphuric acid for several hours. In all cases where the ethereal salts were solid, the residue was crystallised from methylic alcohol and the melting point taken. Oily ethereal salts were hydrolysed, and the melting points of the acids thus obtained were determined. The melting points of recovered acids, in cases where etherification did not take place, or took place to but a slight extent, were also taken.

*Cinnamic Acid, Allocinnamic Acid, and Atropic Acid.*



These three isomeric phenylacrylic acids were first investigated. The cinnamic acid obtained from Kahlbaum melted at 133°. The results, Nos. 1—8, obtained are given in the Table (p. 91).

The ethereal salt, after recrystallisation from methylic alcohol, melted at  $34^{\circ}$  (Anschütz and Kinnicutt, *Ber.*, 1879, 11, 1220, give  $33.4^{\circ}$ ), and the regenerated acid obtained by hydrolysis melted at  $133^{\circ}$  (Kraut, *Annalen*, 1865, 133, 193, gives  $133^{\circ}$ ).

*Allocinnamic Acid*.—Prof. C. Liebermann, of Charlottenberg, was kind enough to provide us with about 2 grams of this acid, and we desire to express our thanks to him for his kindness. The acid melted at  $68^{\circ}$  (Liebermann,  $68^{\circ}$ ). The results, Nos. 9—14, are given in the Table, p. 91.

The oily ethereal salt, after hydrolysis with warm potash, yielded an acid melting at  $66$ — $67^{\circ}$ . It is thus evident that Fischer's method of etherification yields the salt of allocinnamic acid and not of cinnamic acid.

*Atropic Acid*.—This acid, which we obtained from Schucharat, melted at  $106^{\circ}$ . The results, No. 15—22, are given in the Table.

The oily product, after hydrolysis with potash, gave an acid melting at  $105^{\circ}$ .

*Ortho-, Meta-, and Para-nitrocinnamic Acids from Kahlbaum.*

*Orthonitrocinnamic Acid*.—See Table, Nos. 23 and 24.

The ethereal salt, after crystallisation from methylic alcohol, melted at  $73^{\circ}$  (Beilstein and Kuhlberg, *Annalen*, 1872, 163, 126, give  $72$ — $73^{\circ}$ ).

*Metanitrocinnamic Acid*.—See Table, Nos. 25 and 26.

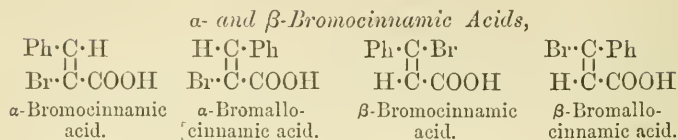
This ethereal salt does not appear to have been described before. It crystallises from methylic alcohol in pale yellow prisms melting at  $123$ — $124^{\circ}$ . It is only sparingly soluble in methylic or ethylic alcohol, and in ether or carbon bisulphide, but dissolves readily in chloroform or benzene.

0.500 gave 28.8 c.c. of moist nitrogen at  $17^{\circ}$  and 757 mm.  $N = 6.65$ .

Theory requires 6.76 per cent.

*Paranitrocinnamic Acid*.—See Table, Nos. 27 and 28.

As the ethereal salt is almost insoluble in ether, the amount formed could not be determined by the usual method. The process we adopted was as follows: water was added at the end of the hour, the precipitate collected, treated with dilute sodium carbonate solution in order to remove any unaltered acid, and then washed, dried at  $100^{\circ}$ , and weighed. After recrystallisation from alcohol, in which it is only slightly soluble, it melted at  $160^{\circ}$  (Kopp, *Jahresbericht*, 1861, 410, gives  $161^{\circ}$ ).



The two *α*-acids were obtained by the method described by Scockmeyer (*Diss.*, 1883), namely, by the action of alcoholic potash on cinnamic acid dibromide, and were separated by fractionally precipitating the solutions of their potassium salts with hydrochloric acid. The *α*-bromocinnamic acid, purified by crystallisation of its sparingly soluble ammonium salt, melted at 131°.

0.200 gave 0.1656 AgBr. Br = 35.21.

$\text{C}_6\text{H}_5 \cdot \text{CH} : \text{CBr} \cdot \text{COOH}$  requires Br = 35.24 per cent.

The results obtained with *α*-bromocinnamic acids, Nos. 29 and 30, are given in the Table (p. 91).

The *α*-bromallocinnamic acid, after purification by recrystallisation from water, was obtained in glistening plates melting at 120°.

0.200 gave 0.1662 AgBr. Br = 35.36. Theory requires 35.24 per cent.

The results obtained with *α*-bromallocinnamic acid, Nos. 31—34, are given in the Table.

As we thought the somewhat high numbers in 31—32 might be due to the presence of a small quantity of the isomeric acid melting at 131°, we took the acid recovered from the above experiments, and determined the amount of ethereal salt formed from this; the results, Nos. 33 and 34, agree with those given above.

The oily ethereal salts, when hydrolysed with cold aqueous potash, yielded an acid melting at 119°. From the fact that it crystallised from water in plates, that it dissolved with the greatest readiness in ammonia, and also from its melting point, the acid thus obtained was undoubtedly the *α*-allo-acid. From this, it is apparent that *α*-bromallocinnamic acid is converted into its true ethereal salt, and not into the isomeric *α*-bromocinnamate, when etherified by Fischer's method; whereas, when its alcoholic solution is saturated with hydrogen chloride, molecular rearrangement occurs, and the salt of *α*-bromocinnamic acid is obtained.

The isomeric *β*-brom-acids were obtained by the method described by Michael and Brown (*Ber.*, 1886, 19, 1379, and 1887, 20, 552), and we are able to confirm their work in every respect; the two acids were separated by crystallisation, first from alcohol and then from chloroform, as these chemists recommend.

The  $\beta$ -bromocinnamic acid melting at  $134\text{--}135^\circ$  crystallises from its chloroform solution on spontaneous evaporation in well-developed cubical crystals.

0.200 gave 0.1645 AgBr. Br = 35.0. Theory requires 35.24 per cent.

The results obtained with this acid, Nos. 35—42, are given in the Table, p. 91.

The oily ethereal salt, on hydrolysis, gave an acid which melted at  $133\text{--}134^\circ$ , after recrystallisation from carbon bisulphide.

*$\beta$ -Bromallocinnamic acid* (see Erlenmeyer, *Annalen*, 1895, 287, 1), melting at  $159^\circ$ , is readily obtained pure after one recrystallisation from a small quantity of alcohol.

0.2044 gave 0.1701 AgBr. Br = 35.42. Theory requires 35.24 per cent.

The results, Nos. 43—48, are given in the Table.

The *methylic* salt crystallises from alcohol in thick, colourless prisms melting at  $58^\circ$ . It is moderately soluble in ethylic alcohol or benzene, and dissolves with great readiness in ether, chloroform or carbon bisulphide.

0.2423 gave 0.1887 AgBr. Br = 33.06.

0.2582 „ 0.2019 AgBr. Br = 33.28.

Theory requires 33.19 per cent.

The ease with which the two  $\beta$ -brom-acids can be obtained pure by following Michael and Brown's directions renders inexplicable such statements as those of Liebermann and Scholz (*Ber.*, 1892, 25, 552) and of Erlenmeyer (*ibid.*, 1886, 19, 1936) that the acid melting at  $133\text{--}134^\circ$  does not exist.

#### *Dichloro-, Dibromo-, and Di-iodo-cinnamic Acids,*

*Dichlorocinnamic Acid*,  $\text{Ph} \cdot \overset{\text{Cl}}{\underset{\text{Cl}}{\text{C}}} \cdot \text{COOH}$  or  $\text{Ph} \cdot \overset{\text{C} \cdot \text{Cl}}{\underset{\text{C} \cdot \text{Cl}}{\text{C}}} \cdot \text{COOH}$ .—This acid

was prepared by saturating a chloroform solution of phenylpropionic acid with chlorine. After recrystallisation from light petroleum, it melted at  $120^\circ$  (Nissen, *Ber.*, 1892, 25, 2665, gives  $120\text{--}121^\circ$ ). The results, Nos. 49 and 50, are given in the Table.

The ethereal salt was obtained in the form of an oil.

*Dibromocinnamic Acids*.—Two isomeric dibrom-acids were obtained by adding bromine to phenylpropionic acid in chloroform solution (Roser and Haselhoff, *Annalen*, 1888, 247, 139); they were separated by dissolving them in a small quantity of chloroform, and adding light

petroleum until a permanent turbidity was produced. The acid melting at  $139^{\circ}$  crystallised first, and was purified by recrystallisation from boiling light petroleum (b. p.  $60-80^{\circ}$ ). The isomeric acid melting at  $100^{\circ}$  was obtained pure only after repeated solution in chloroform and precipitation by light petroleum.

The results with the acid melting at  $139^{\circ}$  (Nos. 51 and 52), and with the acid melting at  $100^{\circ}$  (Nos. 53 and 54), are given in the Table. The acid recovered from the former melted at  $139^{\circ}$ .

*Di-iodocinnamic Acid*,  $\text{CIPh}\cdot\text{CI}\cdot\text{COOH}$ , obtained by the method given by Liebermann and Sachse (*Ber.* 1891, **24**, 4113), after several recrystallisations from chloroform, melted at  $167^{\circ}$ . (L. and S. give  $171^{\circ}$ ). The recovered acid melted at  $170^{\circ}$ . The results, Nos. 55 and 56, are given in the Table (p. 92).

#### *$\alpha$ -Cyanocinnamic Acids.*

*$\alpha$ -Cyanocinnamic acid*,  $\text{Ph}\cdot\overset{\text{H}}{\underset{\text{NC}\cdot\text{C}\cdot\text{COOH}}{\underset{\text{||}}{\text{C}}}}$  or  $\text{H}\cdot\overset{\text{C}}{\underset{\text{CN}\cdot\text{C}\cdot\text{COOH}}{\underset{\text{||}}{\text{C}}}}\cdot\text{Ph}$ , obtained by Carrick's method (*J. pr. Chem.*, 1892, **45**, 401), after recrystallisation from alcohol, melted at  $180^{\circ}$  (Carrick,  $180^{\circ}$ ). See Table, Nos. 57 and 58.

The *methylic* salt thus obtained crystallised from its alcoholic solution in small, colourless prisms melting at  $89^{\circ}$ . It is readily soluble in chloroform or ether, and moderately in alcohol, benzene, and carbon bisulphide.

0.5 gave 31.8 c.c. moist nitrogen at  $13^{\circ}$  and 752 mm.  $\text{N}=7.43$ .

$\text{CHPh}\cdot\text{C}(\text{CN})\cdot\text{COOMe}$  requires 7.48 per cent.

*$\alpha$ -Cyano-orthonitrocinnamic Acid*.—The ethylic salt of this acid was obtained by the action of sodium ethoxide on a mixture of ethylic cyanacetate and orthonitrobenzaldehyde (Riedel, *J. pr. Chem.*, 1896, **54**, 541), and was hydrolysed by the requisite quantity of normal sodium hydroxide at about  $60^{\circ}$ . The acid thus obtained melted at  $223^{\circ}$  (Riedel,  $223^{\circ}$ ). The results obtained are given in Nos. 59 and 60 of the Table.

The recovered acid melted at  $220^{\circ}$ . The *methylic* salt crystallised from alcohol in small, discoloured needles melting at  $142^{\circ}$ .

*$\alpha$ -Cyanometanitrocinnamic acid* was obtained in a similar manner. We find that the ethylic salt melts at  $134^{\circ}$ , and that the melting point is not altered by repeated crystallisation from alcohol. (Riedel gives  $127-128^{\circ}$ ).

0.4 gave 39.4 c.c. moist nitrogen at  $16^{\circ}$  and 761 mm.  $\text{N}=11.5$ .

$\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{C}(\text{CN})\cdot\text{COOEt}$  requires  $\text{N}=11.38$  per cent.



The results, Nos. 61 and 62, obtained with this acid are given in the Table.

The recovered acid melted at 170—171° (Riedel, 172°). The methylic salt, after recrystallisation from alcohol, was obtained in fine, silky needles melting at 135—136°, and readily soluble in the usual solvents.

0.3 gave 30.8 c.c. moist nitrogen at 16° and 762 mm.  $N = 12.0$ .

$\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH} : \text{C}(\text{CN}) \cdot \text{COOMe}$  requires  $N = 12.07$  per cent.

*α-Phenylcinnamic Acids,*



These acids were prepared and separated by Bakunin's method (*Gazz.*, 1897, 27, ii, 48). The yield of allo-acid was extremely small.

The α-phenylcinnamic acid, melting at 172°, gave the results Nos. 63 and 64 of the Table.

The ethereal salt, after recrystallisation from alcohol, melted at 77° (Bakunin, 77°).

The α-phenylallocinnamic acid, after crystallisation from water, was obtained in colourless prisms melting at 136°.

0.5 gram, after 1 hour with 3 per cent. solution, gave 0.2137 gram ethereal salt.

The methylic salt thus obtained was semi-solid, whereas Bakunin, who obtained the same compound by the action of methylic iodide on the silver salt of the acid, describes it as an oil. The solid we obtained apparently contained a considerable amount of the solid ethereal salt of the isomeric α-phenylcinnamic acid, as the acid recovered from this first etherification yielded an oil when treated a second time with the 3 per cent. hydrogen chloride solution. The results are given in Nos. 65 and 66 of the Table. The recovered acid melted at 137—138°.

*α-Phenylorthonitrocinnamic Acids.*—A mixture of the two isomeric acids was obtained by the action of acetic anhydride and sodium phenylacetate on orthonitrobenzaldehyde (Bakunin, *Gazz.*, 1895, 25, i, 137). The α-phenylorthonitrocinnamic acid,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH} : \text{C}(\text{H}) \cdot \text{COOH}$  was readily obtained pure by Bakunin's method. It melted at 195—196°, and on etherification gave the results Nos. 67 and 68 of the Table. The ethereal salt, after recrystallisation from alcohol, melted at 75° (Bakunin, 75—76°).

A mixture of the above acid with the isomeric allo-acid was obtained by Bakunin's method; it melted at  $155^{\circ}$ , whereas the pure allo-acid melts at  $146\text{--}147^{\circ}$ . We adopted the following method for its purification. The mixture of acids was boiled for 1 hour with a 5 per cent. solution of hydrogen chloride in methylic alcohol, 20 c.c. of this solution being used for each gram of the mixed acids; after etherification, the solution was poured into water, extracted with ether, and the ethereal solution washed with sodium carbonate solution; on the addition of hydrochloric acid to this alkaline solution, the  $\alpha$ -phenylorthonitroalloeinnamic acid,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{C} \cdot \text{H}$   
 $\text{COOH} \cdot \text{C} \cdot \text{Ph}$ , was thrown down, and after recrystallisation from dilute acetic acid melted at  $146^{\circ}$ .

Whether the results, Nos. 69 and 70 in the Table, are somewhat too high owing to the presence of a small quantity of the isomeric acid, we cannot at present say with any degree of certainty, as the yield of allo-acid is extremely poor and we had but a gram or so at our disposal.

*$\alpha$ -Phenylmetanitrocinnamic Acids.*—The two acids were obtained by Bakunin's method (*loc. cit.*). The  $\alpha$ -phenylmetanitrocinnamic acid melted at  $181^{\circ}$  and gave the results Nos. 71 and 72 in the Table (p. 92). The ethereal salt, after recrystallisation from alcohol, melted at  $72^{\circ}$ .

*$\alpha$ -Phenylmetanitroallocinnamic acid* melted at  $196^{\circ}$ . The results, Nos. 73 and 74, obtained with this acid are given in the Table.

*$\alpha$ -Phenylparanitrocinnamic acid* melting at  $214^{\circ}$  gave the results Nos. 75 and 76 of the Table. The ethereal salt crystallised from alcohol in yellow needles melting at  $141\text{--}142^{\circ}$  (Bakunin,  $141\text{--}142^{\circ}$ ).

*$\alpha$ -Phenylparanitroallocinnamic acid* melted at  $144^{\circ}$  (Bakunin,  $142^{\circ}$ ). For results, see Nos. 77 and 78 of Table. The recovered acid melted at  $144^{\circ}$ .

*Triphenylacrylic acid*,  $\text{CPh}_2 \cdot \text{CPh} \cdot \text{COOH}$ , was prepared from the acid amide (Heyl and Meyer, *Ber.*, 1896, 29, 2786) by a method very similar to that adopted by Heyl and Meyer, except that we used the amide, in a fine state of division, suspended in dilute sulphuric acid, and kept the mixture well stirred by an automatic stirrer while the nitrite solution was being run in; the acid thus obtained melted at  $213^{\circ}$ . The results of etherification, Nos. 79 and 80, are given in the Table. The unaltered acid melted at  $213\text{--}214^{\circ}$ .

Heyl and Meyer (*loc. cit.*) have already shown that this acid is only slowly etherified when hydrogen chloride is passed for several hours through its solution in boiling methyl alcohol.

*$\beta$ -Di-iodacrylic acid*,  $\text{CHI} \cdot \text{CI} \cdot \text{COOH}$ .—This acid was prepared by the addition of iodine to propiolic acid, as described by Bruck (*Ber.*, 1891, 24, 4120); after recrystallisation from chloroform, it melted at about  $76^{\circ}$ , but after recrystallisation from water at  $104^{\circ}$  (Bruck,  $104^{\circ}$ ).

Table of Results.

No. of experiments.	Name of acid.	Amount of acid.	Strength of methyl alcoholic solution of HCl.	Amount of HCl solution.	Time.	Amount of ethereal salt formed.	Per cent. of acid converted into ethereal salt.
		gram.	per cent.	c.c.	mins.	gr.	
1	Cinnamic.	0.5	3	10	60	0.5425	99.12
2	Do.	0.5	3	10	60	0.5447	99.54
3	Do.	0.5	3	10	10	0.4958	90.60
4	Do.	0.5	3	10	10	0.4982	91.02
5	Do.	0.5	1	10	60	0.5433	99.28
6	Do.	0.5	1	10	60	0.5459	99.74
7	Do.	0.5	1	10	30	0.4996	91.28
8	Do.	0.5	1	10	30	0.5033	91.96
9	Allocinnamic.	0.5	3	10	60	0.5282	96.52
10	Do.	0.5	3	10	60	0.5304	96.92
11	Do.	0.5	3	10	10	0.4269	78.00
12	Do.	0.5	3	10	10	0.4261	77.86
13	Do.	0.5	1	10	60	0.4820	88.06
14	Do.	0.5	1	10	30	0.4692	85.73
15	Atropic.	0.5	3	10	60	0.5102	93.22
16	Do.	0.5	3	10	60	0.5112	93.40
17	Do.	0.5	3	10	10	0.3420	62.50
18	Do.	0.5	3	10	10	0.3421	62.52
19	Do.	0.5	1	10	60	0.4442	81.16
20	Do.	0.5	1	10	60	0.4408	80.54
21	Do.	0.5	1	10	30	0.2989	54.62
22	Do.	0.5	1	10	30	0.3023	55.23
23	Orthonitrocinnamic.	0.5	3	10	60	0.3176	59.22
24	Do.	0.5	3	10	60	0.3195	59.58
25	Metanitrocinnamic.	0.5	3	10	60	0.5227	97.48
26	Do.	0.5	3	10	60	0.5203	97.02
27	Paranitrocinnamic.	0.5	3	10	60	0.5223	97.40
28	Do.	0.5	3	10	60	0.5218	97.30
29	$\alpha$ -Bromocinnamic.	0.5	3	10	60	0.4091	77.06
30	Do.	0.5	3	10	60	0.4038	76.06
31	$\alpha$ -Bromallocinnamic.	0.5	3	10	60	0.1312	24.72
32	Do.	0.5	3	10	60	0.1302	24.52
33	Do.	0.5	3	10	60	0.1332	25.09
34	Do.	0.5	3	10	60	0.1312	24.72
35	$\beta$ -Bromocinnamic, m. p. 134—135°.	0.5	3	10	60	0.5291	99.68
36	Do.	0.5	3	10	60	0.5308	100.00
37	Do.	0.5	3	10	60	0.5256	99.02
38	Do.	0.5	3	10	60	0.5281	99.48
39	Do.	0.5	1	10	60	0.4666	87.90
40	Do.	0.5	1	10	60	0.4698	88.50
41	Do.	0.5	1	10	30	0.4222	79.54
42	Do.	0.5	1	10	30	0.4231	79.70
43	$\beta$ -Bromallocinnamic, m. p. 159°.	0.5	3	10	60	0.5241	98.74
44	Do.	0.5	3	10	60	0.5260	99.08
45	Do.	0.5	1	10	60	0.4648	87.56
46	Do.	0.5	1	10	60	0.4630	87.22
47	Do.	0.5	1	10	30	0.4165	78.46
48	Do.	0.5	1	10	30	0.4154	78.26

*Table of Results—(continued).*

No. of experiments.	Name of acid.	Amount of acid.	Strength of methyl alcoholic solution of HCl.	Amount of HCl solution.	Time.	Amount of ethereal salt formula.	Per cent. of acid converted into ethereal salt.
		gram.	per cent.	c.c.	mins.	gr.	
49	Dichlorocinnamic.	0.5	3	10	60	0.1645	30.90
50	Do.	0.5	3	10	60	0.1615	30.34
51	Dibromocinnamic, m. p. 139°.	0.5	3	10	60	0.0414	7.92
52	Do.	0.5	3	10	60	0.0428	8.19
53	Dibromocinnamic, m. p. 100°.	0.5	3	10	60	0.0700	13.38
54	Do.	0.5	3	10	60	0.0687	13.13
55	Di-iodocinnamic.	0.5	3	10	60	0.0109	2.10
56	Do.	0.5	3	10	60	0.0102	1.96
57	$\alpha$ -Cyanocinnamic.	0.5	3	10	60	0.3466	64.14
58	Do.	0.5	3	10	60	0.3472	64.24
59	$\alpha$ -Cyano-orthonitrocinnamic.	0.5	3	10	60	0.2677	50.32
60	Do.	0.5	3	10	60	0.2702	50.78
61	$\alpha$ -Cyanometanitrocinnamic.	0.5	3	10	60	0.3203	60.20
62	Do.	0.5	3	10	60	0.3176	59.70
63	$\alpha$ -Phenylcinnamic.	0.5	3	10	60	0.3981	74.94
64	Do.	0.5	3	10	60	0.4013	75.54
65	$\alpha$ -Phenylalloccinnamic.	0.5	3	10	60	0.0631	11.88
66	Do.	0.5	3	10	60	0.0596	11.22
67	$\alpha$ -Phenylorthonitrocinnamic.	0.5	3	10	60	0.3974	75.55
68	Do.	0.5	3	10	60	0.3982	75.70
69	$\alpha$ -Phenylorthonitroalloccinnamic.	0.5	3	10	60	0.0813	15.45
70	$\alpha$ -Phenylorthonitroalloccinnamic.	0.5	3	10	60	0.0795	15.11
71	$\alpha$ -Phenylmetanitrocinnamic.	0.5	3	10	60	0.3829	72.79
72	Do.	0.5	3	10	60	0.3849	73.17
73	$\alpha$ -Phenylmetanitroalloccinnamic.	0.5	3	10	60	0.0744	14.14
74	Do.	0.5	3	10	60	0.0710	13.53
75	$\alpha$ -Phenylparanitrocinnamic.	0.5	3	10	60	0.3746	71.21
76	Do.	0.5	3	10	60	0.3804	72.32
77	$\alpha$ -Phenylparanitroalloccinnamic.	0.5	3	10	60	0.0684	12.99
78	Do.	0.5	3	10	60	0.0657	12.48
79	Triphenylacrylic.	0.5	3	10	60	0.0112	2.14
80	Do.	0.5	3	10	60	0.0124	2.37
81	$\alpha\beta$ -Di-iodacrylic.	0.5	3	10	60	0.0387	7.42
82	Do.	0.5	3	10	60	0.0352	6.75

The results obtained with this acid, Nos. 81 and 82, are given in the Table. The recovered acid melted at 103–104°.

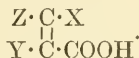
*Discussion of Results.*

From the results of the experiments described in the preceding pages, we consider ourselves justified in drawing the following conclusions.

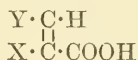
1. Unsaturated acids which, in addition to an  $\alpha$ -substituting group, also contain a radicle in the *cis*-position relatively to the carboxylic group, that is, acids of the type



are difficult to etherify when boiled for an hour with a 3 per cent. solution of hydrogen chloride in methylic alcohol. The same property is also characteristic of acids in which the third hydrogen atom of acrylic acid is replaced by a substituting group



2. Di-substituted acrylic acids in which one group is in the  $\alpha$ -position and the other in the *trans*-position relatively to the carboxylic group, are readily etherified under the conditions given above.



This remarkable difference in behaviour supplies us with a simple method of determining the configurations of stereoisomeric acids,  $\text{CHX}:\text{CY} \cdot \text{COOH}$ , where X and Y may be alike or dissimilar. We require merely to boil half a gram of each acid with 10 c.c. of a 3 per cent. solution of hydrogen chloride in methylic acid, and determine which acid yields the larger percentage of ethereal salt. This acid will be the one with the substituting group in the *trans*-position, and the acid which yields little or no ethereal salt will have the substituting group in the *cis*-position.

We also think it probable that this difference on etherification may be made use of in the separation of such stereoisomeric acids, in very much the same manner as Martz (*Ber.*, 1894, 27, 3147) and Jannasch and Weiler (*ibid.*, 3447) have been able to separate diortho-substituted benzoic acids from their isomerides. The separation in the acrylic series will not be so complete as in the benzoic, as, according to our results, the difference on etherification is not so marked as in the benzoic series. We have found that the method can be used with advantage in the separation of  $\alpha$ -phenylallocinnamic acid from  $\alpha$ -phenyleinnamic acid, and it can undoubtedly be used with equal



advantage in the separation of the corresponding nitro-acids. The method adopted by Bakunin (*loc. cit.*) for the purification of these acids is lengthy and tedious, and can probably be considerably curtailed by the process of etherification. We may point out that our results confirm in a remarkable manner the constitutions of the  $\alpha$ -phenylcinnamic acids arrived at by Bakunin from entirely different considerations.

3. Substituted acrylic acids in which the substituting groups are only in the  $\beta$ -position are readily etherified under the conditions given above. As examples of this generalisation, we have the two  $\beta$ -bromocinnamic acids, both of which yield over 90 per cent. of ethereal salt. We are at present engaged in preparing  $\beta\beta$ -diiodacrylic acid, and hope shortly to be able to state that this obeys the same law.

4. The results we have obtained with mono-substituted acrylic acids are somewhat too meagre for us to draw general conclusions with any degree of certainty; those, however, which we have so far obtained by using more dilute solutions of hydrogen chloride, namely, a 1 per cent., in methylic alcohol, seem to indicate that an  $\alpha$ -substituted acrylic acid is more difficult to etherify than the isomeric  $\beta$ -compound. In support of this, we have the fact that atropic acid ( $\alpha$ -phenylacrylic acid) is more difficult to etherify than either of the  $\beta$ -phenylacrylic acids (cinnamic and allocinnamic acid). This conclusion is further supported by Anschütz's results (*Ber.*, 1897, 30, 2652). Anschütz finds that mesaconic acid,  $\begin{array}{c} \text{Me} \cdot \text{C} \cdot \text{COOH} \\ | \\ \text{COOH} \cdot \text{C} \cdot \text{H} \end{array}$ , when boiled for a short time

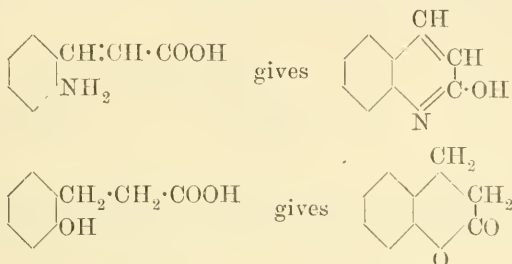
with a 0.5 per cent. solution of hydrogen chloride, yields the monomethylic salt,  $\begin{array}{c} \text{Me} \cdot \text{C} \cdot \text{COOH} \\ | \\ \text{COOMe} \cdot \text{C} \cdot \text{H} \end{array}$ .

The differences between cinnamic and allocinnamic acids point to the conclusion that a  $\beta$ -substituted acrylic acid, in which the substituting radicle is in the *cis*-position relatively to the carboxylic group, is more difficult to etherify than the isomeric *trans*-compound. We give these generalisations with the greatest reserve, as further investigations with other acids, for example, crotonic acids, are necessary to prove whether they are correct.

5. The radicle weights or volumes of the substituting groups in the  $\alpha$ - and *cis*-positions appear to be an important factor in determining the actual amount of ethereal salt formed in each case. A survey of the results obtained with dichloro-, dibromo-, and di-iodo-cinnamic acids brings out this generalisation with great clearness. The dichloro-acid yields more ethereal salt than either of the two dibromo-acids, and these again yield more than the di-iodo-acid. This conclusion is entirely in accordance with V. Meyer's work on diortho-substituted benzoic acids, and with that of Kellas (*Z. physik. Chem.*, 1897, 24,

221) on mono-substituted benzoic acids, and also with our own on substituted benzamides (Trans., 1895, 233).

6. The presence of a nitro-group in the ortho-position in certain cinnamic acids, for example, in orthonitrocinnamic acid itself, and also in  $\alpha$ -cyano-orthonitrocinnamic acid, appears to have a retarding influence on the formation of the ethereal salt. This is in complete harmony with a suggestion made by Victor Meyer and one of us several years ago, but which received no support from actual experiment conducted at that time (*Ber.*, 1895, 28, 1267). It is a well known fact that ortho-substituted cinnamic and hydrocinnamic acids readily undergo condensation, yielding ring compounds. For example,

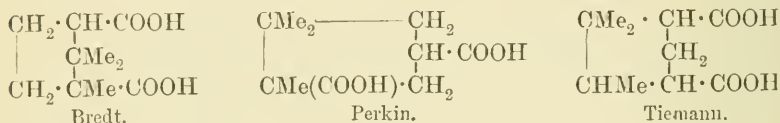


The fact that the isomeric meta- and para-compounds undergo no similar condensations is supposed to be due to the fact that, in these acids, the substituting groups are not sufficiently near to the carboxylic group to allow of the elimination of  $\text{H}_2\text{O}$ ,  $\text{HBr}$ , &c. The results we have obtained may be due to the fact that the nitro-group is in closer proximity to the carboxylic group in the ortho-acids than in the meta- and para-acids, and this may account for the retardation. If so, we should expect to meet the same phenomenon in all ortho-substituted cinnamic acids, and also in diortho-substituted cinnamic acids. This is a point which we consider deserves a little more attention, and we purpose studying a number of these acids.

7. The results we have obtained by the etherification of allocinnamic acid and  $\alpha$ -bromallocinnamic acid indicate that Fischer's method of etherification yields the ethereal acids of the allo-acids, and not those of the more stable isomeric acids. This is an extremely interesting point, since other authorities state that these allo-acids, when their alcoholic solutions are saturated with hydrogen chloride and allowed to stand, yield the ethereal salts of the more stable acids.

8. In the introduction to this paper, we stated that one of the reasons for undertaking the investigation was to account for the characteristic behaviour of camphoric acid on etherification by the aid of the stereochemistry of the acid molecule. As the result of our

investigation, we are able to state that in *unsaturated* acids a carboxylic group which has substituting groups in the  $\alpha$ - and *cis*-positions with respect to itself is difficult to etherify. It is true that in Bredt's formula for camphoric acid, and also in the newer formula suggested by W. H. Perkin, jun. (Proc., 1897, 218), one of the carboxylic groups is thus situated, it has substituting groups in the  $\alpha$ - and also in the *cis*-position. The other carboxylic group in camphoric acid is not so situated; it has a substituting group in the *cis*-position, but none in the  $\alpha$ -position. We consider, then, that our results render the behaviour of camphoric acid on etherification explicable if we adopt either Bredt's or Perkin's formula. The same remarks, however, do not apply to Tiemann's formula (*Ber.*, 1895, 28, 1079):



The great difference is that camphoric acid is a ring compound, whereas our researches have been limited to aliphatic unsaturated acids.

9. The results we have obtained are in complete harmony with the configurations of unsaturated acids according to the van't Hoff-Wislicenus theory, and we consider that they establish with certainty the conclusion previously arrived at, namely, that in what are usually termed *cis*-substituted monocarboxylic acids the substituting group is in closer proximity to the carboxylic group than when it is in the *trans*-position.

In conclusion, we may state that, having obtained such interesting results with monocarboxylic acids, we at once turned our attention to dibasic acids. From a private communication from Professor Anschütz, we learn that he has already taken up the study of a number of such acids in the direction indicated in the *Berichte*, and we have therefore not investigated any of these acids ourselves.

The question whether generalisations similar to those we have obtained for unsaturated acids may not also hold, to some extent, for saturated acids immediately presented itself to us, and the fact that such acids as dibromosuccinic acid, dibromhydrocinnamic acid and its nitro-derivatives, are difficult to etherify indicates that interesting results may probably be obtained in this direction.





Aug. Kekulé



## KEKULÉ MEMORIAL LECTURE.\*

(DELIVERED ON DECEMBER 15th, 1897.)

By FRANCIS R. JAPP, F.R.S.

THE great chemist whose life and work I shall endeavour to pass in brief review before you this evening, was not one of the popular heroes of science. Whatever may have been his qualifications for playing such a part—and surely, great natural eloquence, unfailing lucidity, and a humour that enlivened the discussion of even the driest subjects, are to be thus regarded—he apparently disdained to put them to so ignoble a use as the achievement of mere popular fame. He brought an intellect of incomparable power and subtlety to bear on problems so abstruse, so remote from the everyday thoughts and interests of mankind, that the vast majority even of educated persons have never heard either of the problems, or of the man who did so much to solve them. The greater, then, is the need that we, who realise both the direct scientific value of Kekulé's work and the furthering influence which, in spite of its apparent remoteness, it has exercised indirectly on the welfare of mankind, should place on record our sense of his high deserts.

Friedrich August Kekulé—he made use of only the second of his Christian names—was born at Darmstadt on September 7th, 1829.† His father was a Hessian *Oberkriegsrath*. Even as a boy, Kekulé displayed remarkable powers; at the Gymnasium of his native town he distinguished himself in mathematics and in drawing; whilst outside the school curriculum his instincts as an observer found congenial scope in the study of the flora and butterflies of the district. After passing the leaving examination at the Gymnasium in 1847, he determined, in accordance with his father's wish, to become an architect, and for this purpose entered as *studiosus architecturæ* at the University of Giessen. Kekulé, in later life, by no means regarded the time thus spent as wasted; he always laid stress on the turn which the study of architecture had given to his thoughts; on the necessity which he ever afterwards felt of having before him, if possible, an actual picture of any problem he was dealing with. He was doubtless right. After

\* Chemical Society's Memorial Lectures, No. VII.

† For the facts of Kekulé's life I am indebted partly to two obituary notices: one by Wallach (*Naturwissenschaftliche Rundschau*, 1896, **13**, 437) and the other by Königs (*Münchener Medicinische Wochenschrift*, 1896, **39**, 920); and partly to Kekulé's well known address delivered before the German Chemical Society in 1890 on the occasion of the *Kekuléfeier*.

all, he remained an architect to the last : only it was the architecture of molecules, instead of that of buildings, with which it was his lot to concern himself.

In any case, chemists may feel thankful that Kekulé's architectural studies led him to the University, instead of into an architect's office. Liebig was then at Giessen ; Kekulé attended his lectures on chemistry ; and such was the fascination both of the lecturer and of the subject, that the young student resolved to abandon architecture and devote himself entirely to chemistry. His relatives insisted that he should take sufficient time to consider his decision ; and he therefore returned to his native town, where he spent a semester studying at the Polytechnic School. At the end of that time he returned to Giessen and entered the University Laboratory as a pupil of Liebig and Will. His first research, carried out under Will's guidance, was an investigation of amylsulphuric acid and its salts, published in 1850. About this time, Liebig offered Kekulé an assistantship, which, however, he declined, as he was enabled, through the generosity of a stepbrother, a merchant in London, to study for a year in Paris. Here he remained from 1851 to 1852, attended Dumas' lectures, and made the acquaintance of Wurtz, Cahours, Regnault and others. Of most influence on the formation of Kekulé's views, however, was the friendship which he formed with Gerhardt, the originator of the type theory, whose great *Traité de Chimie Organique*, then just ready for the press, he was allowed to read in manuscript. On returning to Germany, he graduated as Doctor of Philosophy at Giessen in 1852. He then obtained his first appointment, that of private assistant to Baron von Planta, at whose beautifully situated château, Reichenau, near Coire, in Switzerland, he spent a year and a half. He published, jointly with von Planta, two papers on the action of ethylic iodide on nicotine and coniine, and some elaborate analyses of Swiss mineral waters ; the latter work can hardly have been very congenial to Kekulé, who, as he afterwards said, was employing the leisure and freedom from distractions which his post afforded, in elaborating the ideas which he had found in Gerhardt's unpublished manuscript. In January, 1854, he exchanged his assistantship with von Planta for a similar post with Stenhouse in London. Here he became intimate with Williamson and Odling, both of whom, but especially the former, exercised great influence on the development of his ideas. He says :

"If in Paris I had an opportunity of acquainting myself with Gerhardt's unpublished views, I had now the good fortune to enter into active friendly intercourse with Williamson and to familiarise myself with the modes of thought of this philosophical intellect.

"Originally a pupil of Liebig, I had become a pupil of Dumas, Gerhardt, and Williamson : I no longer belonged to any school."

The training which Kekulé received during these *Wanderjahre* was undoubtedly the best he could possibly have had for the task he was destined to perform. Suppose that, instead of going to Paris, he had been shortsighted enough to accept the assistantship which Liebig offered him. In that case he might have shared the fate of many promising students who have been promoted to be the assistants of their teachers; he might have gone on producing research work cut to a single pattern; he might have become a *Privatdocent* in the institution in which he was trained; and so on to the end of the chapter. Not that a man of Kekulé's originality and strength of intellect could ever have been satisfied to play the part of a mere scientific hodman; but had he been hampered by a one-sided training, it might have been much longer before he discovered where his strength as a reformer lay: in fact he might not have discovered it at all until the brief period—the too brief period—during which the great creative geniuses of science really create, was in his case past. A Kekulé trained solely in Liebig's laboratory would never have adopted the masterful attitude of the actual Kekulé towards the doctrines of the school of Berzelius; and although he might have excited the ire of some of his opponents less, organic chemistry would have moved more slowly.

Kekulé always emphasised the necessity for getting rid of preconceptions due to early training. "Free yourselves from the spirit of the school," he said; "you will then be capable of doing something of your own. Remember that it was Mephisto who gave the Scholar the advice:

Am besten ist's auch hier, wenn Ihr nur Einen hört  
Und auf des Meisters Worte schwört."

A few months after his arrival in London Kekulé published his well-known "Note on a new Series of Organic Acids containing Sulphur" (*Annalen*, 1854, 90, 309; *Proc. Roy. Soc.*, 1856, 7, 37—received April 5, 1854). This paper is noteworthy as the first published work of Kekulé's which exhibits his distinctive modes of thought. Various passages contained in it clearly show that, although only briefly indicated, at least the germ of his later system, the linking of atoms in terms of their valency, was present to his mind. I will illustrate this more fully later on when I come to deal with Kekulé's theoretical views. Meanwhile, in the present merely historical connection, the interesting passage from his speech delivered before the German Chemical Society (*Ber.*, 1890, 23, 1306) on the occasion of celebrations held in his honour, in which he describes the origin of the idea of the linking of atoms, may be quoted. The local colour should commend it to a London audience.

"During my stay in London I resided for a considerable time in Clapham Road in the neighbourhood of the Common. I frequently, however, spent my evenings with my friend Hugo Müller at Islington, at the opposite end of the giant town. We talked of many things, but oftenest of our beloved chemistry. One fine summer evening I was returning by the last omnibus, 'outside,' as usual, through the deserted streets of the metropolis, which are at other times so full of life. I fell into a reverie (*Träumerei*), and lo, the atoms were gambolling before my eyes! Whenever, hitherto, these diminutive beings had appeared to me, they had always been in motion; but up to that time I had never been able to discern the nature of their motion. Now, however, I saw how, frequently, two smaller atoms united to form a pair; how a larger one embraced two smaller ones; how still larger ones kept hold of three or even four of the smaller; whilst the whole kept whirling in a giddy dance. I saw how the larger ones formed a chain, dragging the smaller ones after them, but only at the ends of the chain. I saw what our Past Master, Kopp, my highly honoured teacher and friend, has depicted with such charm in his 'Molekularwelt'; but I saw it long before him. The cry of the conductor: 'Clapham Road,' awakened me from my dreaming; but I spent a part of the night in putting on paper at least sketches of these dream forms. This was the origin of the *Strukturtheorie*."

Then he relates a similar experience of how the idea of the benzene theory occurred to him. This refers to a later period, when Kekulé was professor in Ghent, but may be quoted here in connection with the previous passage. He describes how he was at work one evening:

"I was sitting, writing at my text-book; but the work did not progress; my thoughts were elsewhere. I turned my chair to the fire and dozed. Again the atoms were gambolling before my eyes. This time the smaller groups kept modestly in the background. My mental eye, rendered more acute by repeated visions of the kind, could now distinguish larger structures, of manifold conformation: long rows, sometimes more closely fitted together; all twining and twisting in snake-like motion. But look! What was that? One of the snakes had seized hold of its own tail, and the form whirled mockingly before my eyes. As if by a flash of lightning I awoke; and this time also I spent the rest of the night in working out the consequences of the hypothesis.

"Let us learn to dream, gentlemen," adds Kekulé, "then perhaps we shall find the truth . . . but let us beware of publishing our dreams before they have been put to the proof by the waking understanding."

After his return from England, Kekulé went to Heidelberg, where on February 29th, 1856, he obtained the *venia legendi* in Chemistry at the University. The young *Privatdocent* fitted up a modest laboratory consisting of a room with a kitchen adjoining it. Among the few students whom he could accommodate was Adolf Baeyer, who there carried out his well-known work on the organo-arsenic compounds. Kekulé himself prepared the experiments and most of the specimens for his lectures on organic chemistry. Generally the last item of his



hard day's work was the sweeping out of the class room against next morning's lecture.

The various investigations which Kekulé published about this time, excellent as they were from an experimental point of view, were still more remarkable for the theoretical conceptions which they embodied; indeed, in the latter respect, as every chemist knows, they inaugurated a new era in organic chemistry. The two papers on the constitution of mercuric fulminate (1857 and 1858); that on the so-called conjugated compounds and the theory of polyatomic radicles (1857), which contains a complete system of multiple types and mixed types based on this theory; those on the conversion of acetic acid into glycolic acid and on chloralide (1858) and finally, the celebrated paper "On the Constitution and Metamorphoses of Chemical Compounds and on the Chemical Nature of Carbon" (*Annalen*, 1858, 106, 293), which contained a full statement of Kekulé's views on the linking of atoms—the foundation on which our modern system of constitutional formulæ rests—attracted the attention of chemists throughout the world, with the result that, in 1858, Kekulé, on Stas's recommendation, was called as ordinary professor of chemistry to the University of Ghent.

It might have seemed that the inspiring influence of a great chemist and teacher had thus been lost to Kekulé's fatherland. But this was not the case. Thanks to the fact that in Germany a student need not have studied at the university at which he graduates, German students are attracted to teachers rather than to institutions; in fact, in their peregrinations from one university to another, they resemble the wandering scholars of former days. Many young Germans thus made the pilgrimage to Ghent to study under Kekulé: among their number Baeyer, Glaser, Hübner, Körner, Ladenburg, Linnemann and Wichelhaus.\* Later on, these disciples, as teachers in the German universities, were instrumental in disseminating Kekulé's doctrines.

The nine years which Kekulé spent in Ghent were years of great productivity. In the theoretical papers which he had up to that time published, he had laid down the lines of his future work—nay, of the future work of the organic chemists of his generation. That work would consist in experimentally verifying the innumerable predictions, and in considering the further logical consequences, of his theory.

Of the investigations belonging to this period may be mentioned: those on organic acids, their basicity and hydricity (atomicity); on the relations between succinic, malic, and tartaric acids; on the isomeric unsaturated dibasic acids—fumaric and maleic acids on the one hand, and mesaconic, citraconic and itaconic acids on the other—a marvellous piece of experimental work, in which, however, Kekulé was less for-

\* Among English chemists, Dewar and G. Carey Foster studied under Kekulé in Ghent.



fortunate than usual in the interpretation of his results, although, considering the complexity of the problem, this was not to be wondered at; the conversion of hydroxy-acids into bromo-acids; the electrolysis of dibasic acids; the synthesis of acids of the benzene series by the replacement of bromine in bromobenzenes by carboxyl; the elucidation of the constitution of azo- and diazo-compounds, and the transformation of diazo- into azo-compounds. The theoretical work is of course for the most part involved in the practical and cannot be discussed apart from it. One piece of theoretical work must, however, be specially mentioned. It is Kekulé's benzene theory—the crowning achievement of the doctrine of the linking of atoms. Of this, more will be said later on.

A new system of chemistry is not a proposition in Euclid, to be proved in a few words; its proofs are cumulative, and its truth or error—or to speak more accurately, its expediency or in expediency—can be tested only by applying it to the whole body of the science. This is why so many of the great originators in our science have bent their minds to the task of writing a text-book. The text-books of Lavoisier, Berzelius, Gerhardt, Kolbe and Kekulé are cases in point.

The publication of Kekulé's *Lehrbuch der organischen Chemie* falls for the most part within the Ghent period. The first instalment appeared in 1859. The effect produced by the book was enormous. The facts of organic chemistry appeared to group themselves spontaneously under the new system. Whatever might be its ultimate fate, here was a method of exposition immeasurably superior to any that had preceded it; and as a result, every text-book of organic chemistry that has since appeared has shown more or less distinctly the influence of this remarkable work. Even Kolbe's accusation that the method owed its success to the fact that it saved chemists the trouble of thinking, may be regarded as indirect praise.

Kekulé's *Lehrbuch* was never finished. The first instalment of the third volume appeared in 1867—the year in which Kekulé left Ghent—after which further publication ceased for thirteen years. On one occasion, Kekulé received from his students an amusing reminder that they desired to see the continuation of the work. It was at a *Commerz* held at Bonn in the early seventies. For the benefit of those who may be unfamiliar with German academic customs, I may explain that the *Commerz* is a students' festivity in which the beer of the country plays an important part. Professors are frequently present by invitation, and just as, at the ancient *saturnalia*, the position of master and servant was reversed, so, at these mild modern *saturnalia*, there is a certain relaxation of the attitude of strict respect which the German student otherwise maintains towards his professor. Thus a professor may hear his work, or some literary or

other controversy in which he is engaged, playfully discussed in a set of occasional verses, or made the theme of a humorous dramatic interlude enacted by the students. On the occasion referred to, Kekulé, on taking his seat, found on the table in front of him what purported to be a complete, bound copy of the only partially existent third volume of his *Lehrbuch*. On closer examination it proved to be a box, in book form, containing writing materials. Kekulé enjoyed the joke, but declined to take the hint, at least for the time being. Later on, in 1880, with the collaboration of Anschütz and Schultz, he returned to the work; but with the conclusion of the third volume this second attempt also collapsed.

In 1867 Kekulé was appointed to the Professorship of Chemistry in the University of Bonn. Here he found himself at the head of a palatial laboratory, built shortly before from Hofmann's designs. During the first part of the time which he spent at Bonn his scientific activity continued, and he published various important researches, chiefly in collaboration with pupils. Among the numerous chemists who studied under Kekulé at Bonn may be mentioned: Anschütz, Bedson, Bernthsen, Carnelley, Claisen, Dittmar, Franchimont, van't Hoff, Klinger, Königs, G. Schultz, Thorpe, Wallach, and Zincke. The research work belonging to this period deals with the following subjects, amongst others: phenylmercaptan and phenylic sulphide (investigated jointly with Szuch); ethylbenzoic acid (with Thorpe); the formation of hydroxyazobenzene by the action of diazobenzene chloride on sodium phenoxide (with Hidegh); an aromatic glycolic acid—hydroxymethylbenzoic acid—(with Dittmar); the condensation products and polymeric modifications of aldehyde (with Zincke); the action of phosphorus pentachloride on sulphonic acids (with Gibertini and Barbaglia); on triphenylmethane (with Franchimont); the formation of cymene and cymyl hydrosulphide by the action of phosphorus pentasulphide on camphor (with Pott and Flesch), and of cymene by the action of iodine on oil of turpentine (with Bruylants); the constitution of the allyl compounds and of crotonic acid (with Rinne); and the well-known speculations on the constitution of isatin and isatic acid, which led, later on, to the synthesis of these compounds by Claisen and Shadwell. About the year 1876, however, Kekulé's physical powers began to show signs of failure, and for the rest of his life he practically never again enjoyed a continuance of good health. He aged prematurely and rapidly. Increasing deafness exercised a depressing effect upon him, and led him to shun the society even of his more intimate friends. Under these circumstances it is not surprising that the time which he devoted to his laboratory was greatly curtailed. There was still, however, an

occasional but unfailing incentive to research ; namely, the publication, by other chemists, of results which clashed with his theoretical views. In such cases, Kekulé's suspicions of the accuracy of the observations were at once aroused ; the work was carefully repeated and shown to be vitiated by some blunder ; in fact, the effect of the corrected work was generally to establish Kekulé's views more securely than ever. Cases in point are the re-investigation of Tanatar's "bioxyfumaric acid" and "trioxymaleic acid," which proved to be racemic acid and mesotartaric acid respectively, published jointly with Anschütz in 1880—81 ; of Gruber and Barth's "carboxytartronic" (dihydroxytartaric) acid in 1883 ; and of Carius' "trichlorphenomalic" (trichlor- $\beta$ -acetylacrylic) acid, jointly with Strecker, in 1884. The whole of this work, both experimental and theoretical, is masterly, finished in all its details, worthy of Kekulé at his best. How the supposed "carboxytartronic" acid, up to that time regarded as a pillar of Ladenburg's prism formula for benzene, was shown to be dihydroxytartaric acid and to furnish fresh evidence in favour of Kekulé's hexagon ; how "trichlorphenomalic" acid, first discovered by Carius and furnished by him with a wrong formula and various self-contradictory reactions, then apparently abolished by Krafft, was finally rehabilitated, explained, and summoned as a fresh witness on behalf of the hexagon : these narratives are, to those capable of following them, of absolutely dramatic interest. Of this dramatic interest none was more conscious than Kekulé himself ; he calls the story of "trichlorphenomalic" acid a "Comedy of Errors."

Kekulé's premature physical decay was, therefore, entirely unaccompanied by any corresponding failure of his mental powers. These remained fresh to the last. Even up to a few months before his death, he would, when his strength permitted, discuss with his assistants problems connected with the recent progress of chemical science.

There is no doubt that Kekulé had presumed too much on a naturally strong constitution and had undermined it by excessive study in early life. In the speech already referred to, he admits as much. I will quote the passage and also that immediately following it, which contains much excellent advice to young students :

"I have faithfully followed the counsel which my old master, Liebig, gave me when I was a young beginner. 'If you want to be a chemist,' Liebig said to me when I was working in his laboratory, 'you will have to ruin your health ; no one who does not ruin his health with study will ever do anything in chemistry nowadays.' That was forty years ago. Is it still true ? I faithfully followed the advice. During many years I managed to do with four and even three hours' sleep. A single night spent over my books did not count ; it was only when two or three came in succession that I thought I had done

anything meritorious. At that time I had acquired such a fund of knowledge as to make my friends think that I was more trustworthy than the *Jahresbericht*.

"Those good days are long past. Of the various mental powers, imagination is the first to go ; memory follows—fortunately, slowly ; the longest to remain is the critical faculty, but this may still do good service, provided that it rests on the broad foundation of solid knowledge acquired by thorough industry. May I draw a moral ? I would recommend my young fellow-chemists to be diligent during youth.

"One cannot explore new countries in express trains, nor will the study of even the best text-books qualify a man to become a discoverer. Whoever is content to follow well-laid promenades until he reaches some pleasant eminence frequented by tourists, may, by striking into the thickets, gather some forgotten flower ; or, if cryptogams, mosses, and lichens satisfy him, may even bring home a well-filled vasculum ; but anything essentially new he will not find. Whoever wishes to train himself as an investigator must study the travellers' original works ; and that, too, so thoroughly that he is able to read between the lines—to divine the author's unexpressed thought. He must follow the paths of the Pathfinders ; he must note every footprint, every bent twig, every fallen leaf. Then, standing at the extreme point reached by his predecessors, it will be easy for him to perceive where the foot of a further pioneer may find solid ground."

These words were spoken on the occasion of what, I believe, was Kekulé's last appearance before a public audience. The German Chemical Society had resolved to celebrate the twenty-fifth anniversary of the publication of Kekulé's benzene theory. To this end they held, in his honour, on March 11th, 1890, a festival of a magnificence perhaps unparalleled in the history of science. Chemical Societies in all parts of the world—our own, as the oldest, heading the list—united in sending delegates with addresses of congratulation. A portrait of Kekulé had been painted by H. von Angeli at the instance of the German coal tar colour manufacturers, who had adopted this means of testifying to their sense of the influence which Kekulé's theoretical views had exercised in furthering their branch of chemical industry ; this portrait, which is now in the National Gallery in Berlin, was unveiled on that occasion. The President of the Society, A. W. von Hofmann, delivered one of these felicitous addresses of which I fear that the secret, so far as chemists are concerned, has died with him : in it he sketched the history of benzene from the time of its discovery as "bicarburetted hydrogen" by Faraday up to the point when Kekulé appeared, to "pluck the heart out of its mystery." Then A. von Baeyer gave a critical review of the entire field of the benzene theory, coming to the conclusion that all lines of discussion of the problem ultimately led to the solution first furnished by Kekulé. Other distinguished pupils of Kekulé's added their tribute of homage. Finally the master himself replied, in a speech which was, beyond



cavil, the culminating point of the day's proceedings, striking as these had been. It was the personal utterance of a man whose utterances had hitherto been confined mainly to the exposition of the impersonal facts and theories of his science. It was modestly autobiographical; it traced the growth and training of the speaker's powers; it afforded a glimpse into his intellectual workshop. Needless to say that it produced a profound impression. I have already given copious extracts from this speech; I only wish that time permitted me to quote the whole. It should be read by every one who desires to understand Kekulé's character and influence.

On the day preceding these celebrations, Kekulé communicated verbally \* to the German Chemical Society, at the ordinary meeting of March 10th, 1890, the results of the last scientific investigation on which he was ever engaged. It was an experimental proof of the absence of a para-bond in pyridine, and was doubtless intended to have an indirect bearing on his benzene formula.

A chill which Kekulé received in April, 1896, on a journey to Cassel, told on his already weakened system. The state of his health began to occasion the gravest fears. At the same time symptoms of heart disease manifested themselves. However, his health again improved; but just when the immediate danger appeared to have passed over, he succumbed to failure of the heart's action on July 13th, 1896.

Kekulé's merits never lacked recognition. He was a member of most of the European academies and other learned societies. He was elected a Foreign Member of our own Society in 1862, and of the Royal Society in 1875. He received the Copley Medal in 1885, and the Prussian *Ordre pour le Mérite* in 1895. The present German Emperor, who, during his period of study at Bonn, was a pupil of Kekulé, revived an old title of nobility which Kekulé's family had formerly borne; and during his later years the great chemist signed himself Kekule † von Stradonitz. Posterity, however, will probably prefer to know him by the name under which the work of his life was published.

Great as were Kekulé's powers as a thinker and an investigator, it is no exaggeration to say that he was equally distinguished as a teacher, whether in the lecture room or in the laboratory. His speech was of extraordinary ease and precision. His lectures, which were delivered, so far as my recollection goes, without notes, might have been published in the form in which they were spoken. His

\* The memoir does not appear to have ever been written; at all events it was not published in the *Berichte*. A statement of the interesting results obtained, privately communicated by Kekulé himself, is, however, to be found in Anschütz's edition of Richter's *Organische Chemie*, 2, 1896, pp. 518—520.

† The acute accent on the final *e* is dropped.



ideas were always ready at his call ; thus when, in directing the work of research students, the chances of an investigation brought him upon some subject which he could not possibly have been previously considering, his exposition was as sure and as logical as in his set lectures, and save that he naturally made much freer use of colloquialisms, might, like the lectures, have been written down as it stood. The effect of his discourse was heightened by a natural play of humour, of a somewhat dry and caustic type, for the exercise of which the opinions of scientific opponents and the blunders of students equally afforded scope. He was invariably fresh and stimulating ; one detected no trace of that listlessness which is so frequently the bane of speakers who are compelled to lecture year after year on the same theme to what is practically the same audience of average students. He had, moreover, the advantage of a striking personal appearance ; and his face, ordinarily of a grave and reflective cast, lighted up when he spoke. His laboratory teaching, in which, during his later years at all events, he devoted himself almost exclusively to directing the work of research students, was remarkable for the way in which he endeavoured to awaken independent thought in the student ; thus he did not dictate a particular course to be carried out blindly by the student, and resent any suggestion as an impertinence—a method of teaching not unknown in some laboratories where the output of research work is possibly in excess of its educational value ; on the contrary, he was never better pleased than when a student was full of suggestions, which he would spend much time in patiently listening to and criticising. The one thing which he never pardoned in a student was want of interest in his work ; such a student was, for the future, quietly ignored.

If one compares Kekulé's published experimental work with that of many other eminent chemists among his fellow-countrymen—with that, for example, of Liebig, or Wöhler, or Hofmann—one is struck by its much smaller volume. His ill-health affords only a partial explanation. Although no one acquainted with Kekulé's extraordinary powers of work would dream of taxing him with indolence, yet the whole of his career unmistakably showed that with him work was a means and not an end. He began by formulating certain important theoretical conceptions, and he then, for a time, exerted himself to verify them experimentally. But when he saw that his ideas had taken root, and that hundreds of willing disciples were engaged in this task of verification ; when he realised that only by such general co-operation could the work be brought to a successful issue ; he contented himself, for the most part, with looking on and criticising. As he said, the critical faculty was, of the various mental powers, that which survived longest. His criticism, as we have seen, frequently took the

useful form of the correction of inaccurate observations. Again, with a view to disseminating his doctrines, he began to write his text-book. But long ere the text-book was finished, it had done its work; the doctrines were almost universally received; and the text-book remained a noble fragment.

After all, Kekulé's supreme merit lies in his contributions to theoretical chemistry. There is, here as elsewhere, a necessary division of labour, and it is irrational to complain that the intellectual gifts of a Kekulé do not include those of a Hofmann—that a Lavoisier is not also a Scheele.

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It now remains to consider, somewhat more fully than has been possible in the course of the foregoing brief sketch of Kekulé's life, the main features of his theoretical work. But here a two-fold difficulty arises.

Kekulé's greatest achievements in theoretical chemistry are: the doctrine of the linking of atoms in terms of their valency, and, growing out of this, the theory of the structure of organic molecules, both in open-chain and in closed-chain compounds. Even the youngest branch of these theories—that dealing with the structure of closed-chain or cyclic compounds—has been before the world more than thirty years. Moreover, they are not recondite theories, hidden away in the depths of the science; on the contrary, they are organic chemistry itself, and our students learn them on their first introduction to the subject. In addressing an audience, therefore, of expert chemists, what new thing can be said on these well-worn themes?

The only admissible course is to take up the question of origins. Here the second difficulty presents itself.

Great theoretical conceptions are not created out of nothing. Not only is, in most cases, the substratum of experimental or observational fact on which they rest previously on record; but later historical research generally discloses the presence, scattered throughout the literature of the subject, of anticipatory germs of the theories themselves. This commonplace in the history of science finds expression in the saying that "the theory was in the air." Hence arise the innumerable claims to priority, with some of which I fear I must deal on the present occasion.

As a preliminary to the discussion of the theoretical conceptions which we owe to Kekulé, it will be necessary to consider briefly the state of organic chemistry at the time when he came upon the scene.

The dualistic electro-chemical theory elaborated by Berzelius, which for many years had dominated the entire field of chemistry, had, so far as organic chemistry was concerned, fallen before the attacks of

Dumas, Laurent, and the other supporters of the doctrine of substitution. In 1842, Melsens showed that trichloroacetic acid could be reconverted into acetic acid; and Berzelius, compelled at length to admit that the two compounds belonged to the same class, made a noteworthy concession to the doctrine of substitution. Unable to accept without qualification the view that elements so widely separated in the electro-chemical scale as hydrogen and chlorine could mutually replace one another in compounds without materially changing the properties of the latter, he devised the doctrine of conjugated compounds, and limited the operation of this process of substitution to the conjuncts. Thus acetic acid and trichloroacetic acid were conjugated oxalic acids in which the respective conjuncts were  $C_2H_3$  and  $C_2Cl_3$ ;



According to Berzelius, the replacement of hydrogen by chlorine, as long as it was confined to the conjunct, did not materially change the properties of the compound.

This limitation of the action of substitution to the conjuncts, and indeed the entire theory of conjugated compounds, has generally been looked upon as an unconscious subterfuge, adopted by Berzelius to cover his retreat. I think, however, that, regarded even from the standpoint of our modern electro-chemical theories, the limitation appears a perfectly legitimate one. The error in Berzelius' original system was an error of excess: it had arisen from applying conceptions drawn from the behaviour of electrolytes, or ionisable compounds, to non-electrolytes, or non-ionisable compounds. In making the limitation just referred to, Berzelius merely withdrew the previous undue extension of his system, whilst retaining the portions which still held good. It is precisely when a halogen atom replaces hydrogen of the conjunct—that is, of the hydrocarbon radicle of a compound—that it is not ionisable; and it is only when the substituents are non-ionisable that the Dumas-Laurent statement of the law of substitution is valid. I mention this, because it appears to me that, in this matter, Berzelius hardly received justice from his opponents. Kekulé, for example, ridiculing Berzelius' change of front, says (*Lehrbuch*, 1, 74—75): "That which had been absurd as long as it was regarded without any hypothesis, became 'surprisingly clear and simple' when seen through the medium of the hypothesis of the conjuncts . . . In his joy over the conjuncts, he [Berzelius] had forgotten that his object was to combat the theory of substitution."

The chief point, however, is that Berzelius and his school were thus compelled to abandon their doctrine of the unchangeable nature of compound radicles.

Kolbe, the great continuator of Berzelius' system, adopted and extended this doctrine of the conjuncts. At the same time he introduced the conception of more complex radicles (*nähere Radicale*) which were built up from simpler radicles (*entferntere Radicale*). Thus, according to Kolbe, acetic acid contains a conjugated radicle,  $C_2H_3\text{---}C_2$  (called by Kolbe "acetyl") consisting of carbon conjugated with methyl; this unites with oxygen to form  $C_2H_3\text{---}C_2O_3$ , acetoxyl; and the latter in turn combines with water to form acetic acid,  $C_2H_3\text{---}C_2O_3.HO$ . This view of the constitution of acetic acid is, as will be seen, not far removed from that now held; it clearly indicates that one half of the carbon in the molecule is present as methyl, whilst the other half serves to satisfy the affinity of oxygen.

Kolbe's extraordinary power of expressing chemical reactions in terms of chemical constitution was unfortunately coupled with an almost complete inability to realise the force of arguments drawn from physical laws. One result was that until 1870 he continued to use Gmelin's equivalents instead of our present atomic weights. There can be little doubt that this both hampered his efficiency as an investigator and prevented his theoretical views from being received at their full value. Kolbe, however, afterwards contended that his mistaken adherence to the old equivalents had facilitated his discovery of the constitution of acids, aldehydes, and ketones, and his prognosis of secondary and tertiary alcohols.

Thanks mainly to the conceptions of chemical structure which we owe to Kekulé, we can, looking back on the disputes which raged round the radicle theory, perceive where truth lay, and where error; nay, we can often see that, of two competing rational formulæ, both were right, each affording a partial glimpse of a truth which afterwards found its fuller expression in the structural formula of the compound. But Kekulé's predecessors were not in this position, and it is not surprising that the manifold hypotheses, and the contradictions, real or apparent, of the radicle theory led many to regard the problem of the constitution of chemical compounds, at least in the sense in which the supporters of this theory understood it, as insoluble.

Gerhardt was one of those who held this view, and in his earlier exposition of his "unitary system" (1848) he employed empirical formulæ only. His chief efforts were at that time directed to representing the various chemical compounds by comparable quantities—their molecular weights—and for this purpose he selected as his unit the molecular weight of water, the formula of which he wrote  $H_2O$ . He employed our present atomic weights for carbon, oxygen, sulphur and their analogues; but somewhat misleadingly called these atomic weights "equivalents."



The difficulty of dealing with organic compounds by means of empirical formulæ alone, led Gerhardt to extend his original system, and to introduce into the formulæ certain atomic groups which he termed "residues." When two compounds interact, eliminating jointly the elements of water or of some simple inorganic compound, the two residues of the original compounds combine. Thus, in the formation of nitrobenzene from benzene and nitric acid, water is eliminated, and the "benzene residue,"  $C_6H_5$ , unites with the "nitric acid residue,"  $NO_2$ . The so-called residues were thus in many cases identical with the old radicles (leaving out of account the fact that Gerhardt used the new atomic weights), and the system was an attempt to secure the benefits of the radicle theory whilst avoiding its more or less hypothetical basis. The way was thus paved for the union of the radicle theory with Dumas' type theory, the outcome of which union was Gerhardt's type theory.

As regards the latter theory, the idea of the ammonia type was furnished by the researches of Wurtz and Hofmann (1849-50) on the substituted ammonias, in which 1, or 2, or 3 hydrogen atoms of the original ammonia molecule were replaced by alcohol radicles. Williamson (1850) showed that alcohol and ether might in like manner be derived from 1 mol. of water by the replacement of either 1 or 2 hydrogen atoms by such radicles; and in the following year (1851) he adopted a similar view in the case of the acids; thus, he regarded acetic acid as 1 mol. of water in which a hydrogen atom is replaced by acetyl,  $C_2H_3O$ . Shortly afterwards (1852), Gerhardt, applying to the monobasic acids a method analogous to that by which Williamson had effected the synthesis of ether, obtained acetic anhydride and its analogues, which were thus shown to stand in the same relation to the monobasic acids as the ethers to the alcohols.

When once it had been recognised that organic compounds might be derived by substitution (double decomposition) from simple inorganic compounds like water and ammonia, and might therefore be formulated on the *type* or pattern of these, the process of finding other simple inorganic compounds which should serve a similar purpose and so complete the type theory, was a tolerably obvious one. Gerhardt selected, as his four types, hydrogen (free hydrogen was, according to the Laurent-Gerhardt view, a compound,  $H_2$ ), hydrochloric acid, water, and ammonia. The typical formulæ were not intended to indicate the constitution of the compounds as the term was understood by the adherents of the radicle theory. If two compounds belonged to the same type it meant merely that they had in common certain functions and certain modes of formation and decomposition.

The idea of valency, both of elements and of compound radicles, had already been propounded. In his well-known paper "On the



Constitution of Salts" (1851\*), Williamson points out that certain compound radicles, such as  $C_2H_3O$  and  $NO_2$ , can replace 1 atom of hydrogen in 1 mol. of water, giving rise to monobasic acids; whilst others, like  $CO$ ,  $C_2O_2$ , and  $SO_2$ , can replace 2 atoms of hydrogen in 2 mols. of water, yielding dibasic acids. That the linking function of these dyad groups was clearly present to his mind is shown by the following passage (this Journal, 1852, 4, 353) in which, speaking of Wurtz's decomposition of ethylic isocyanate by potassium hydroxide, he says: "One atom of carbonic oxide is here equivalent to 2 atoms of hydrogen, and by replacing them, *holds together* the 2 atoms of hydrate in which they were contained, thus necessarily forming a bibasic compound,  $\begin{matrix} (CO) \\ K_2 \end{matrix} O_2$ , carbonate of potash." This important passage contains the earliest statement of the fact that a double type (here the double water type) is possible only when the compound contains a dyad radicle. Later on, in 1854, Williamson (*Proc. Roy. Soc.*, 7, 11) showed that, by the action of phosphorus pentachloride on sulphuric acid, sulphuryl chlorhydrate and sulphuryl dichloride could successively be obtained, thus proving sulphuric acid to have the formula  $SO_2(OH)_2$  which he had previously assigned to it, but which had been called in question by Gerhardt. In the same year he prepared, jointly with his pupil Kay (*loc. cit.*, p. 135), the tribasic formic ether (ethylic orthoformate),  $CH(OC_2H_5)_3$  by the action of chloroform on sodium ethoxide, and pointed out that it was "a body in which the hydrogen of three atoms of alcohol is replaced by the tribasic radical of chloroform." About the same time, Odling (this Journal, 1855, 7, 1) extended Williamson's views on the constitution of salts and assumed the presence of a triad radicle  $PO'''$  in the acids of phosphorus: thus orthophosphoric acid was formulated on the triple water type as  $\begin{matrix} PO''' \\ 3H' \end{matrix} \} O_3$ . And just as Williamson had shown that the dyad group  $SO_2$  could unite two water residues to form sulphuric acid—a double water type—so Odling employed this same group to unite together a water residue and a sulphuretted hydrogen residue to form thiosulphuric acid—a mixed type; he formulated sodium thiosulphate  $\begin{matrix} SO_2'' \\ 2Na' \end{matrix} \} O'' + S''$ . He thus laid down the conditions under which a mixed type might exist: namely, when the molecule contains a polyad radicle capable of holding together the various residues.† In the same

\* First published in the *Chemical Gazette* for 1851; afterwards reprinted in full in the *Journ. Chem. Soc.*, 1852, 4, 350.

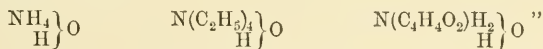
† Ladenburg (*Entwicklungsgeschichte der Chemie*, 2nd ed., p. 232) credits Gerhardt and Chiozza with having, in 1854, derived succinic acid from the mixed type  $NH_3 + H_2O$  in which the two residues were united by the dyad radicle succinyl. In that case these chemists would have anticipated Odling in showing how mixed types

year, Berthelot showed that glycerol formed ethereal salts containing 1, 2 and 3 radicles of a monobasic acid, a result which Wurtz correctly interpreted as proving that glycerol was a trihydric alcohol  $\left. \begin{smallmatrix} \text{C}_3\text{H}_5''' \\ \text{H}_3 \end{smallmatrix} \right\} \text{O}_3$ , formulating it on the triple water type. From this Wurtz was led to foresee the existence of a class of dihydric alcohols, the first member of which, glycol,  $\left. \begin{smallmatrix} \text{C}_2\text{H}_4'' \\ \text{H}_2 \end{smallmatrix} \right\} \text{O}_2$ , he prepared in the following year (1856). Chemists were thus beginning to familiarise themselves with the idea of polyvalent compound radicles of different hydrogen-replacing power.

In the memoir just quoted, Odling employs his well-known valency marks to indicate the valency not only of compound radicles, but also of elements. The conception of a valency of the elementary atoms was introduced into chemistry by E. Frankland in 1852. As Frankland's claims in this respect have been called in question by at least one member of the Kekulé school and were never openly acknowledged by Kekulé himself, I will quote the original passage more fully than would otherwise have been necessary. It occurs at the end of a paper "On a New Series of Organic Bodies containing Metals" (*Phil. Trans.*, 1852, 417). Frankland, who up to that time had been a follower of Kolbe, now criticises unfavourably Kolbe's doctrine of conjugated compounds. After referring to Kolbe's view that cacodyl is "arsenic conjugated with two atoms of methyl,  $(\text{C}_2\text{H}_3)_2\text{As}$ " (Frankland uses Gmelin's equivalents in this paper), and pointing out that the various organo-metallic compounds obviously belong to the same class as cacodyl, he proceeds (*loc. cit.*, p. 439):

"It is generally admitted that when a body becomes conjugated, its essential chemical character is not altered by the presence of the conjunct: thus for instance, the series of acids  $\text{C}_n\text{H}_n\text{O}_4$ , formed by the conjunction of the

should be formulated. What they really say, however, is: "Succinamic acid represents the hydrate of an ammonium in which 2 atoms of hydrogen are replaced by their equivalent of succinyl:



(*Compt. rend.*, 1854, 38, 458), which is a very different matter. Ammonium hydrate is here formulated on the water type, and succinyl replaces two atoms of hydrogen in ammonium: it does not link two residues together. Bearing in mind that, in Part 4, vol. 4 of the *Traité*, Gerhardt formulates the ammonium compounds with pentad nitrogen, it would seem that Ladenburg has read into Gerhardt and Chiozza's formulæ a meaning that was not present to the minds of the authors.

Gerhardt had not grasped Williamson's principle that polyvalent radicles are necessary to link together the residues in multiple types, and in Part 4, vol. 4 of the *Traité* he frequently writes formulæ that are quite at variance with it: thus  $\left. \begin{smallmatrix} \text{C}_3\text{H}_5\text{O} \\ \text{H}_3 \end{smallmatrix} \right\} \text{O}_2$  for glycerol;  $\left. \begin{smallmatrix} \text{C}_7\text{H}_5 \\ \text{H}_3 \end{smallmatrix} \right\} \text{N}_2$  for hydrobenzamide.

radicals  $C_nH_{(n+1)}$  with oxalic acid, have the same neutralising power as the original oxalic acid ; and, therefore, if we assume the organo-metallic bodies above mentioned to be metals conjugated with various hydrocarbons, we might reasonably expect, that the chemical relations of the metal to oxygen, chlorine, sulphur, &c., would remain unchanged ; a glance at the formulæ of these compounds will, however, suffice to show us that this is far from being the case : it is true that cacodyl forms protoxide of cacodyl and cacodylic acid, corresponding to a somewhat hypothetical protoxide of arsenic, which, if it exist, does not possess any well-defined basic character, and the other to arsenious acid ; but no known compound corresponding to arsenic acid can be formed, and yet it cannot be urged that cacodylic acid is decomposed by the powerful reagents requisite to procure further oxidation, for concentrated nitric acid may be distilled from cacodylic acid without decomposition or oxidation in the slightest degree ; the same anomaly presents itself even more strikingly in the case of stanethylum, which, if we are to regard it as a conjugate radical, ought to combine with oxygen in two proportions at least, to form compounds corresponding to protoxide and peroxide of tin ; now stanethylum rapidly oxidises when exposed to the air, and is converted into pure protoxide ; but this compound exhibits none of that powerful tendency to combine with an additional equivalent of oxygen, which is so characteristic of protoxide of tin ; nay, it may even be boiled with dilute nitric acid without evincing any signs of oxidation : I have been quite unable to form any higher oxide than that described ; it is only when the group is entirely broken up and the ethyl separated, that the tin can be induced to unite with another equivalent of oxygen. Stibethyl also refuses to unite with more or less than two equivalents of oxygen, sulphur, iodine, &c., and thus forms compounds which are not represented amongst the combinations of the simple metal antimony.

“ When the formulæ of inorganic chemical compounds are considered, even a superficial observer is struck with the general symmetry of their construction ; the compounds of nitrogen, phosphorus, antimony, and arsenic especially exhibit the tendency of these elements to form compounds containing 3 or 5 equivalents of other elements, and it is in these proportions that their affinities are best satisfied ; thus in the ternary group we have  $NO_3$ ,  $NH_3$ ,  $NI_3$ ,  $NS_3$ ,  $PO_3$ ,  $PH_3$ ,  $PCl_3$ ,  $SbO_3$ ,  $SbH_3$ ,  $SbCl_3$ ,  $AsO_3$ ,  $AsH_3$ ,  $AsCl_3$ , &c. ; and in the five-atom group  $NO_5$ ,  $NH_4O$ ,  $NH_4I$ ,  $PO_5$ ,  $PH_4I$ , &c. Without offering any hypothesis regarding the cause of this symmetrical grouping of atoms, it is sufficiently evident, from the examples just given, that such a tendency or law prevails, and that, *no matter what the character of the uniting atoms may be, the combining power of the attracting element, if I may be allowed the term, is always satisfied by the same number of these atoms.* It was probably a glimpse of the operation of this law among the more complex organic groups, which led Laurent and Dumas to the enunciation of the theory of types ; and had not those distinguished chemists extended their views beyond the point to which they were well supported by then existing facts—had they not assumed that the properties of an organic compound are dependent upon the position, and not upon the nature of its single atoms, that theory would undoubtedly have contributed to the development of the science to a still greater extent than it has already done ; such an assumption could only have

been made at a time when the data upon which it was founded were few and imperfect, and, as the study of the phenomena of substitution progressed, it gradually became untenable, and the fundamental principles of the electro-chemical theory again assumed their sway. The formation and examination of the organo-metallic bodies promise to assist in effecting a fusion of the two theories which have so long divided the opinions of chemists, and which have too hastily been considered irreconcilable; for, whilst it is evident that certain types of series of compounds exist, it is equally clear that the nature of the body derived from the original type is essentially dependent upon the electro-chemical character of its single atoms, and not merely upon the relative position of those atoms. . . .

"Taking this view of the so-called conjugate organic radicals, and regarding the oxygen, sulphur, or chlorine compounds of each metal as the true molecular type of the organo-metallic bodies derived from it by the substitution of an organic group for oxygen, sulphur, &c., the anomalies above mentioned entirely disappear, and we have the following inorganic types and organo-metallic derivatives:—

Inorganic types.	Organo-metallic derivatives.
$As \begin{Bmatrix} S \\ S \end{Bmatrix}$ .....	$As \begin{Bmatrix} C_2H_3 \\ C_2H_3 \end{Bmatrix}$ Cacodyl.
$As \begin{Bmatrix} O \\ O \end{Bmatrix}$ .....	$As \begin{Bmatrix} C_2H_3 \\ C_2H_3 \\ O \end{Bmatrix}$ Oxide of Cacodyl.
$As \begin{Bmatrix} O \\ O \\ O \\ O \end{Bmatrix}$ .....	$As \begin{Bmatrix} C_2H_3 \\ C_2H_3 \\ O \\ O \end{Bmatrix}$ Cacodylic acid.
$Zn \ O$ .....	$Zn \ (C_2H_3)$ Zincmethylum.
$Zn \ \begin{Bmatrix} O \\ O_x \end{Bmatrix}$ .....	$Zn \ \begin{Bmatrix} C_2H_3 \\ O_x \end{Bmatrix}$ Oxide of Zincmethylum.
$Sb \ \begin{Bmatrix} O \\ O \end{Bmatrix}$ .....	$Sb \ \begin{Bmatrix} C_4H_5 \\ C_4H_5 \\ C_4H_5 \end{Bmatrix}$ Stibethine.
$Sb \ \begin{Bmatrix} O \\ O \\ O \\ O \end{Bmatrix}$ .....	$Sb \ \begin{Bmatrix} C_4H_5 \\ C_4H_5 \\ C_4H_5 \\ O \\ O \end{Bmatrix}$ Binoxide of Stibethine.
$Sb \ \begin{Bmatrix} O \\ O \\ O \\ O \end{Bmatrix}$ .....	$Sb \ \begin{Bmatrix} C_4H_5 \\ C_4H_5 \\ C_4H_5 \\ C_4H_5 \\ O \end{Bmatrix}$ Oxide of Stibethylum.
$Sn \ O$ .....	$Sn \ (C_4H_5)$ Stanethylum.
$Sn \ \begin{Bmatrix} O \\ O \end{Bmatrix}$ .....	$Sn \ \begin{Bmatrix} C_4H_5 \\ O \end{Bmatrix}$ Oxide of Stanethylum.
$Hg \ \begin{Bmatrix} I \\ I \end{Bmatrix}$ .....	$Hg \ \begin{Bmatrix} C_2H_3 \\ I \end{Bmatrix}$ Iodide of Hydrargyromethylum."

The foregoing extract from Frankland's paper contains a complete statement, in terms of Gmelin's equivalents, of the valency of the various elementary substances employed as "grouping elements" (to make use of a term introduced later by Frankland) in the formulæ given. In the case of the perissads—nitrogen, phosphorus, arsenic, and antimony—the valencies are 3 and 5, being thus identical with those now assigned to these elements. Arsenic appears in cacodyl as a dyad—a pseudo-dyad, as Frankland would have called it later. In the case of the artiads, zinc and tin, the atomic weight is twice the equivalent; hence the valency given by Frankland must be doubled. Mercury has been taken with the atomic weight 200, and its valency is correctly given.

Another important point is, that Frankland rejects the conception of conjugated compounds and writes typical formulæ explicitly based on the valency of the elements.

One result of Frankland's employing Gmelin's equivalents was that his statement of the law of valency did not impress the adherents of the type theory so much as it might otherwise have done. Kekulé, who in the introduction to his *Lehrbuch* fully acknowledges his obligations to "Williamson and Odling, Hofmann and Wurtz," does not mention Frankland; and a similar omission occurs in Wurtz's *Atomic Theory*. Kekulé, as already mentioned, never expressed himself, at all events in his published writings, on the subject of Frankland's claims; but, if we have not Kekulé's "official" opinion on the subject, we have an opinion, put forward in a paper published by Baeyer in 1858, when the latter was a student in Kekulé's laboratory, which must, I think, be regarded as "semi-official." Baeyer gives a list of compounds formed by the union of monads alone (methyl and chlorine) with the elements of the nitrogen group, in which the latter exhibit either triadic or pentadic character—belonging, as Baeyer expresses it, either to the ammonia type, or to the ammonium chloride type—and adds (*Annalen*, 1858, 105, 274):—

"I would here remind the reader of the series of compounds which Frankland gave in his investigations on zinc-ethyl, in which he drew a parallel between the compounds of the metals with oxygen and those with the alcohol radicles, whilst the latter are analogous to hydrogen and not to oxygen. The view which is thus gained is purely superficial; it vanishes immediately when the proper atomic weight of oxygen is adopted, and the formulæ which contain an odd number of atoms of that element are doubled."

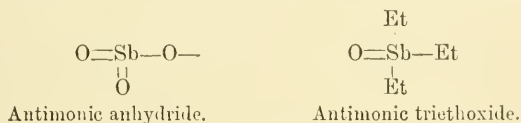
With regard to the foregoing passage, I think we may lay it down as a safe general principle, to be adopted in dealing with this interesting period of chemical history, that a discovery, made by an adherent of the radicle theory and correctly formulated by him in terms of the



old equivalents, does not become the property of the first adherent of the type theory who happens to translate it into the new atomic weights.

Baeyer's criticism has been replied to by Frankland in the introduction to the series of papers on organo-metallic compounds reprinted in his *Experimental Researches* (p. 153). As some chemists may not have seen the passage, I will quote it :—

"Exception has been taken, I think somewhat unfairly [here Baeyer's criticism is given as a footnote], to the analogies upon which, in the following papers, I have founded the doctrine of atomicity. It has been stated, for instance, that there is no real analogy between antimonie anhydride and antimonie triethoxide, if the dyadic atom of oxygen be used in the formula of the first—that the real analogy is between antimonie chloride and antimonie triethoxide, &c. But even in the light of our most recent conceptions of the constitution of chemical compounds, the analogies which I pointed out are strictly correct ; for in antimonie anhydride each atom of antimony has five bonds satisfied by oxygen, whilst in the organo-metallic analogue, antimonie triethoxide, the oxygen of three of these bonds has been replaced by ethyl :



"At the time when the second paper of this chapter was written, I employed, in common with nearly all chemists, what is known as the small atom of oxygen ( $O=8$ ). With this atomic weight oxygen was monadic ; and as it formed the only pentadic inorganic compound of arsenic, it lent itself, on the whole, better to the expression of my analogies than either chlorine, bromine, or iodine ; but (and it is on this ground that I complain of the unfairness of my critic) I distinctly stated \* that I regarded 'the oxygen, sulphur, or *chlorine* compounds of each metal as the true molecular types of the organo-metallic bodies derived from them by the substitution of an organic group for oxygen, sulphur, &c.,' and I actually used, in the table of analogous compounds,  $\text{HgI}_2$  as the type of  $\text{HgMeI}$ ."

If Kekulé did not express himself regarding Frankland's claims, he went further than this, for he claimed to have been himself the first propounder of the doctrine of the valency or, as he termed it, the atomicity, of the elements. In a note "On the Atomicity of the Elements" (*Compt. rend.*, 1864, 58, 510), published in reply to views put forward by Naquet and others, he says : "I consider that it is all the more my duty to intervene in this discussion, seeing that, if I am not mistaken, it was I who first introduced into chemistry the conception of the atomicity of the elements." (It should be mentioned that the first occasion on which Kekulé refers to valency is in his paper on thiacetic acid, published in 1854, two years later than Frankland's

\* See the extract from Frankland's paper already given.

paper.) He then proceeds to combat the doctrine of varying valency: the equivalent of an element may vary; but its valency is as invariable as its atomic weight. Neither is valency to be regarded as identical with maximum capacity for saturation: thus, in reply to Naquet, who regarded iodine as triadic and the elements of the sulphur group, including oxygen, as tetradic, he points out that if iodine is a triad in  $\text{ICl}_3$ , tellurium must be dodecadic in  $\text{TeI}_4$ —a supposed *reductio ad absurdum* which Kekulé's opponents might justly regard as a travesty of their views. He then defines the conditions which, he considers, alone render the determination of the valency of an element possible: the element in question must be combined solely with monads, and the resulting compound must be volatile without decomposition. Such a compound he regards as *atomic*. Two or more atomic molecules may unite to form a *molecular* compound; such a compound may be distinguished by the fact that, when volatilised, it dissociates; it is not available for the purpose of determining the valency of the elements which it contains. Thus  $\text{ICl}$ ,  $\text{PCl}_3$ , and  $\text{NH}_3$ , are atomic compounds, and their formulæ show iodine to be monadic, and phosphorus and nitrogen to be triadic. Iodine trichloride, phosphorus pentachloride, and ammonium chloride are represented as molecular compounds,  $\text{ICl}_3$ ,  $\text{Cl}_2$ ;  $\text{PCl}_3$ ,  $\text{Cl}_2$ ;  $\text{NH}_3$ ,  $\text{HCl}$ . (At that time the existence of phosphorus pentafluoride, a compound of pentadic phosphorus gaseous at ordinary temperatures, and the fact that dry ammonium chloride may be vaporised without dissociation, were, of course, unknown.) Again, referring to his doctrine of fixed valency, he speaks (*loc. cit.*, p. 512) of "the reasoning which has made me remain faithful to my original manner of viewing the subject, and which, I venture to hope, will end by carrying the day against the modifications which have been proposed since." Surely, Frankland's doctrine of varying valency was earlier in the field!

Of all the doctrines which we owe to Kekulé that of fixed valency is probably the one which has met with least acceptance, even among chemists of his own school. At the present day it is, so far as I am aware, without supporters. Yet Kekulé held it to the last.

Whilst we must thus admit that it was with Frankland and not with Kekulé that the idea of the valency of elementary substances originated, we are in a position, I think, to explain how it was that Kekulé came to ignore Frankland's work and to claim the theory for himself. To Kekulé, varying valency and, moreover, varying valency referred to equivalents instead of to atoms, was not valency at all, as he understood it. We must bear in mind the attitude of the two opposed schools in questions of chemical theory: how each seemed to labour under an absolute inability to place itself in the mental position of the other. I have no doubt that Kekulé paid very little atten-

tion to Frankland's theoretical views ; that he evolved the doctrine of valency in part independently and in part from the indications which he found in the writings of Williamson, Odling, and Wurtz ; and that afterwards, perceiving that Frankland had put forward similar ideas, he came to the conclusion that they had not been deduced by a legitimate process and were not correctly stated.

These considerations, which may have appeared important at the time, need not weigh with us at the present day. The battle between the radicle theory and the type theory is long past. The victory was not entirely with either, for the theory of chemical structure, based on the doctrine of valency, absorbed and assimilated both. Frankland correctly perceived that the views which he was advocating promised "to assist in effecting a fusion of the two theories which have so long divided the opinions of chemists, and which have too hastily been considered irreconcilable." But the theory of chemical structure which effected this fusion is imperishably associated with the name of Kekulé, and, therefore, if he did not originate the doctrine of valency, no other chemist used it to so good purpose. Frankland, speaking of valency, says (*Experimental Researches*, p. 154): "I do not forget how much, in its present developments, this law owes to the labours of other chemists, especially to those of Kekulé and Cannizzaro. Indeed, until the latter had placed the atomic weights of the metallic elements on their present consistent basis, the satisfactory development of the doctrine was impossible."

In his later years, Kekulé looked back upon those troublous times with a more tolerant eye. I again quote from his Berlin address :

"No science has developed so steadily as chemistry, although during one period of its development which fell partly within my own experience, the very opposite seemed for a time to be the case. Fifty years ago, the stream of chemical progress had divided into two branches. The one flowed, chiefly on French soil, through luxuriant flower-decked plains ; and those who followed it, with Laurent and Dumas at their head, could reap, during the whole voyage, almost without effort, an abundant harvest. The other followed the course indicated by an old and approved guide-post set up by the great Swedish chemist, Berzelius ; it led for the most part through broken boulders, and only later on did it again reach fertile country. At length, as the two branches had again approached much nearer to one another, they were separated by a thick growth of misunderstandings, so that those who were sailing along on the one side neither saw those on the other, nor understood their speech. Suddenly a loud shout of triumph resounded from the host of the adherents of the type theory. The others had arrived—Frankland at their head. Both sides saw that they had been striving towards the same goal, although by different routes. They exchanged experiences ; each side profited by the conquests of the other ; and with united forces they sailed onward on the reunited stream. One or two held themselves apart and sulked ; they thought

that they alone had held the true course—the right fair-way—but they followed the stream.

“Our present opinions do not, as has frequently been asserted, stand on the ruins of earlier theories. None of the earlier theories has been recognised by later generations as entirely false; all, when stripped of certain ill-proportioned, meaningless excrescences, could be utilised in the later structure, and form with it one harmonious whole.

“Here and there a seed may have lain in the ground without germinating; but everything that grew came from seed that had been previously sown. My views also have grown out of those of my predecessors and are based on them. There is no such thing as absolute novelty in the matter.”

I have allowed the protagonists to speak for themselves, and so great is their agreement, at least in their later utterances, that it seems almost superfluous to call in the aid of an umpire. For the sake of completeness, however, I venture to do so. Ladenburg, although a pupil of Kekulé and thoroughly imbued with his master's teaching, has displayed, in his well-known historical treatise, a most praiseworthy spirit of impartiality in dealing with the various questions at issue between the adherents of the radicle and the type theories. Referring to Frankland's enunciation of the doctrine of valency already quoted, he says (*Entwicklungsgeschichte der Chemie*, 2nd ed., p. 251):—

“With this memoir of Frankland's the first step was taken towards a reconciliation of the hitherto opposed schools—the means was furnished for a mutual understanding. This means was destined to lead to a fusion of the different opinions, and out of the fusion the theory of valency developed. It was a gain for the adherents of the type theory to have secured Frankland's adhesion to their principles; for he brought with him ideas foreign to their modes of thought and capable of being turned to excellent account. I will not assert that the former school could not have taken the final great step—the differentiation of the atoms in terms of their valency—independently; but, having regard to the course which the development actually followed, the influence of Kolbe, and especially of Frankland, on the representatives of the Gerhardt-Williamson school (Wurtz, Kekulé and Odling) can hardly be mistaken. The efforts of both schools were necessary to impart to formulæ the significance which they afterwards acquired.”

I have treated this question of the authorship of the doctrine of valency at considerable length; but the subject seemed to me by its importance to justify this, especially in the present connection, seeing that the whole of Kekulé's work is based on this doctrine.

We must now pass on to consider the use which Kekulé made of the ideas which he found scattered throughout the writings of his predecessors; how he added to them; and how he welded the whole



into the coherent system which forms our present theory of the structure of organic compounds.

Kekulé's first published work of theoretical importance was, as has already been mentioned, his "Note on a New Series of Organic Acids containing Sulphur" (*Annalen*, 1854, 90, 309). He treats various organic compounds of the water type, such as acetic acid and acetic anhydride, with the sulphides of phosphorus, and in this way replaces the typical oxygen by sulphur. He compares the action with that of the chlorides of phosphorus and significantly remarks: "One sees, indeed, that the decomposition is essentially the same; only, when the chlorides of phosphorus are employed, the product breaks up into chloride of ethyl [acetylic chloride] and hydrochloric acid, or into two atoms of chloride of ethyl, as the case may be; whereas, on employing the sulphur compounds of phosphorus, both groups remain united, *because the quantity of sulphur equivalent to 2 atoms of chlorine is not divisible.*" Elsewhere, in the same paper, he refers this difference to "the *dibasic* nature of sulphur." He then proceeds to defend Gerhardt's new atomic weights, and declares the formulæ written with these to be a better expression of the facts than the prevailing formulæ. He says: "It is not merely a difference in the mode of writing, it is an actual fact, that 1 atom of water contains 2 atoms of hydrogen and only 1 atom of oxygen; and that the quantity of chlorine equivalent to *one* atom of oxygen is divisible by 2, whereas sulphur, like oxygen itself is *dibasic*, so that 1 atom is equivalent to 2 atoms of chlorine."

We thus see that the theory of the linking of atoms and groups by means of polyad radicles was already present to Kekulé's mind. Moreover, as was always the case with him, the thought is expressed with such precision and emphasis, as to render it impossible for even the least attentive reader to overlook his meaning.\*

After this apparently unconditional acceptance of Gerhardt's atomic weights, it may surprise us to find Kekulé returning in his next published work to the use of Gmelin's equivalents. The same concession to the prevailing usage was, however, made by other members of the Gerhardt-Williamson school whenever they were merely stating experimental results, or explaining theories for the understanding of which the new atomic weights were not required. Later on, in adopting the new atomic weights, the adherents of this school used, as is well known, crossed symbols for the artiads, thus:  $\text{C} = 12$ ,  $\text{O} = 16$ , as proposed by Williamson, partly in order to indicate

\* Kolbe's well-known hostile criticisms on Kekulé's literary style deal almost exclusively with verbal points; they seldom touch the meaning, which indeed Kolbe's own preconceptions prevented him from grasping. This, it need hardly be said, is written in no spirit of detraction of Kolbe's own work and influence.



that the atom was in these cases equal to twice the equivalent, and partly to avoid confusion with the uncrossed symbols which were employed by the opposed school to denote the old equivalents. Kekulé continued to use these crossed symbols until 1867. How liable to misinterpretation these concessions to the prejudices of opponents were, and how little gratitude they evoked, may be seen from the accusations which Kolbe (*J. pr. Chem.*, 1881, [ii], 24, 398) brings against Kekulé: firstly, of having until 1857 held the view that the old equivalents were identical with the true atomic weights, whereas we have seen that as early as 1854 Kekulé had perfectly clear views to the contrary, although he for some time continued to use the equivalent formulæ for purposes of exposition; and secondly, of afterwards, "until 1867, attributing the atomic weight 16, not, strictly speaking, to the single oxygen atom, but to the double oxygen atom  $\Theta$ ." Kolbe goes on to state that he himself adopted the new atomic weights in 1870, and draws the comforting conclusion that Kekulé anticipated him in this course by only three years!

The first of these papers in which Kekulé reverts to the use of the old equivalents is entitled "On the Constitution of Fulminic Acid" (*Annalen*, 1857, 101, 200), and was followed a year later by a second paper on the same subject. The experimental work was difficult and dangerous. The conclusion at which Kekulé arrived, namely, that fulminic acid is nitroacetonitrile is no longer held by chemists; but the work is of great interest. Perhaps the most important point in the paper is a tabular arrangement of compounds of the marsh gas type: the earliest enunciation of the tetravalency of carbon. After ascribing to mercuric fulminate the formula  $C_2(NO_4)(C_2N)Hg_2$ , Kekulé adds (*loc. cit.*, p. 204):

"This formula shows at the first glance that mercuric fulminate exhibits in its composition the closest analogy with a large number of known compounds, to which, for example, chloroform,  $C_2 H Cl Cl Cl$ , belongs. We might regard it as nitrated chloroform in which the chlorine is replaced partly by cyanogen and partly by mercury.

"The following compounds may be referred to the same type:

$C_2$	$H$	$H$	$H$	$H$	Marsh gas.
$C_2$	$H$	$H$	$H$	$Cl$	Methylic chloride, &c.
$C_2$	$H$	$Cl$	$Cl$	$Cl$	Chloroform, &c.
$C_2$	$(NO_4)$	$Cl$	$Cl$	$Cl$	Chloropicrin.
$C_2$	$(NO_4)$	$(NO_4)$	$Cl$	$Cl$	Marignac's oil.
$C_2$	$(NO_4)$	$Br$	$Br$	$Br$	Bromopicrin.
$C_2$	$H$	$H$	$H$	$(C_2N)$	Acetonitrile.
$C_2$	$Cl$	$Cl$	$Cl$	$(C_2N)$	Trichloroacetonitrile.
$C_2$	$(NO_4)$	$Hg$	$Hg$	$(C_2N)$	Mercuric fulminate.
$C_2$	$(NO_4)$	$H$	$H$	$(C_2N)$	Hypothetical fulminic acid.

“ . . . In assigning these compounds to the same type, I do not use the word in the sense which it bears in Gerhardt's unitary theory, but in that in which it was first employed by Dumas on the occasion of his fruitful investigations on the subject of types. I wish essentially to indicate the relations in which the said compounds stand to one another; that the one, under the influence of appropriate agents, can be produced from, or transformed into, the other.”

I have quoted this passage somewhat fully because Kolbe (*J. pr. Chem.*, 1881, [ii], 23, 374, footnote) has denied that Kekulé here refers mercuric fulminate to the marsh gas type and, indeed, that the passage affords any justification for ascribing to Kekulé the enunciation of the marsh gas type and of the tetravalency of carbon. He bases this denial on Kekulé's statement that he uses the word “type” in Dumas' sense (“mechanical type”) and not in Gerhardt's sense (“chemical type”). Why this statement should deprive Kekulé of all right to the theory which he so clearly expresses in his formulæ, Kolbe does not explain, unless, indeed, the explanation is to be found in a reference which he makes a little further on (*loc. cit.*, p. 375) to Kekulé's paper “On the So-called Conjugated Compounds,” and in which, speaking of Kekulé's direct statement that carbon can be shown to be “tetrabasic or tetratomic,” he says: “He nevertheless feels so uncertain of his ground, that he still hesitates to add the type ‘marsh gas’ to Gerhardt's three types.”

The meaning of Kekulé's remark about types, which Kolbe has, it seems to me, entirely mistaken, is perfectly clear if we view it by the light of the various statements on the subject of types to be found in Kekulé's writings. Kekulé's types (compare *Annalen*, 1857, 104, 132; *Lehrbuch*, 1, 116—117), even when outwardly identical with Gerhardt's “chemical types,” were in reality “mechanical types”: that is, they were based solely on the valency of the constituent elements. Thus, whereas Gerhardt classed the hydrogen type,  $\text{HH}$ , and the hydrochloric acid type,  $\text{HCl}$ , as distinct *chemical* types, Kekulé, looking upon them as *mechanical* types, regarded the latter as merely a special case of the former. Applying this to the matter under consideration, it is evident, that, if Kekulé had employed Gerhardt's types, he could not have tabulated the foregoing compounds in the way he did, as they would not have belonged to the same type. Thus, if he had followed Gerhardt, marsh gas would have belonged to the hydrogen type, methylic chloride to the hydrochloric acid type, and so on; and the parallelism which Kekulé wished to indicate would have been completely hidden. It was, therefore, necessary for him not merely to tabulate the compounds on the marsh gas type, but, seeing that he had used the word “type,” to obviate any possible misunderstanding by stating that he did not mean Gerhardt's types.\*

\* Kolbe also argues (*loc. cit.*) that, in the passage just quoted, Kekulé refers marsh gas to the chloroform type, not chloroform to the marsh gas type. To

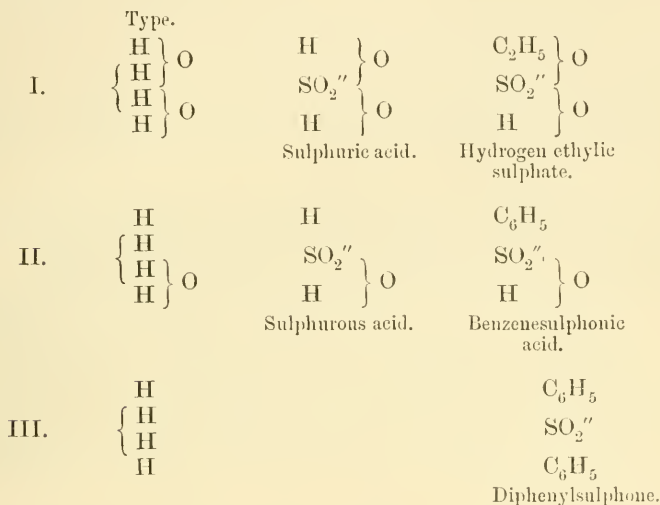
The foregoing demonstration of the tetravalency of the double equivalent of carbon,  $C_2$  (which, as we have seen, meant for Kekulé the atom  $C=12$ ), is obviously incomplete, as it holds good only for the limited class of compounds derivable from methane by the replacement of the hydrogen atoms by the same number of monad radicles. It contains no suggestion of the law of mutual linking of carbon atoms and can at most be regarded as the germ of Kekulé's later theory.

In the same year, Kekulé published an important theoretical paper: "On the So-called Conjugated Compounds and the Theory of Polyatomic Radicles" (*Annalen*, 1857, 104, 129). As the question is entirely one of valency and there are no experimental results to state, he uses Gerhardt's atomic weights, although in three experimental papers published the following year he again reverts, for the last time, however, to the old equivalents. In the introduction to the paper he states that the views which he advocates have, in great part at least, no claim to originality: they are an extension of ideas incidentally put forward by Williamson and forming what might be termed his "theory of polyatomic radicles"; ideas which had already been extended by Odling in his paper "On the Constitution of Acids and Salts," and which had been adopted, although not in a strict form, by Gerhardt in the fourth volume of his *Traité*. Kekulé divides the elements into monobasic or monatomic, dibasic or diatomic, and tribasic or triatomic, and points out that the three principal types—hydrogen, water and ammonia—follow from this classification. In a footnote he adds (*loc. cit.*, p. 133): "Carbon is, as may easily be shown, and as I shall explain in detail on a later occasion, tetrabasic or tetratomic: that is, 1 atom of carbon  $C=12$  is equivalent to 4 atoms of H." He shows that, as regards the so-called conjugated compounds, there is no need to refer these to a separate class: their constitution may be expressed in terms of the valency of the radicles, simple and compound, which they contain. We have already seen, however, that this view of the nature of conjugated compounds had been clearly stated by

disprove this it is only necessary to point out that in the table of compounds which "may be referred to the same type," the formula of chloroform is given *under* that of marsh gas. Kolbe apparently understands the words "referred to the same type" to mean "referred to the same type as chloroform," whereas the sense is: "may all be referred to one and the same type," namely the type that heads the list. This is clearly shown both by the context and by the way in which the words "same type" are again used after the table of compounds.

Kolbe put himself completely out of court in any discussion involving a knowledge of Kekulé's writings, by the statement that he did not consider them worthy of serious attention. In his historical study: *Meine Betheiligung an der Entwicklung der theoretischen Chemie* (*J. pr. Chem.*, 1881, [ii], 23, 377) he says: "In this connection I have had occasion for the first time to read attentively Kekulé's *Lehrbuch*, especially the historical and theoretical chapters. Until then, I had only glanced hastily through it, as I perceived that I could learn nothing useful from it."

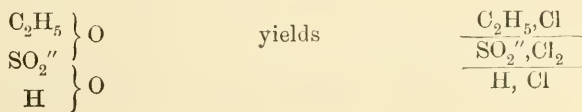
Frankland in 1852. Kekulé, starting, as he premises, with the theory of multiple types and mixed types containing polyvalent radicles, as expounded by Williamson and Odling, develops it into a complete system, laying special stress on the fact that these classes of types are possible only when such polyvalent radicles are present. Thus, of compounds containing the divalent radicle  $\text{SO}_2$ , he gives:



"Compound radicle" is understood in Gerhardt's sense of "a residue left unattacked in any particular reaction," and the "basicity" (valency) of these radicles is deduced from the number of atoms, greatly differing from the radicles themselves in chemical character, with which they combine.

This introduction of the radicles into the types, which must at the time have appeared to place the type theory on a firm basis, was destined to render that theory unnecessary.

Another point worthy of note is the way in which Kekulé uses the action of the chlorides of phosphorus to distinguish between the water type and the hydrogen type. Developing an idea to be found in his memoir on thiactic acid, he points out, that, in the case of the water type, two atoms of chlorine replace one atom of typical oxygen, causing the compound to break up into two atomic groups, whereas the hydrogen type is not acted upon and remains intact. Thus



whereas



In the foregoing paper, Kekulé accepts the radicles (residues) in the form in which he received them from his predecessors and empirically deduces their valency from a study of their compounds. In his great theoretical paper, published the following year (*Annalen*, 1858, 106, 129), "On the Constitution and Metamorphoses of Chemical Compounds, and on the Chemical Nature of Carbon"—a paper which is the foundation of our present theories of organic chemistry—he goes to the root of the matter. He says:—

"I regard it as necessary and, in the present state of chemical knowledge, as, in many cases, possible, to explain the properties of chemical compounds by going back to the elements themselves which compose these compounds. I no longer regard it as the chief problem of the time, to prove the presence of atomic groups which, on the strength of certain properties, may be regarded as radicles; and in this way to refer compounds to a few types, which can hardly have any significance beyond that of mere pattern formulæ. On the contrary I hold that we must extend our investigation to the constitution of the radicles themselves; that we must ascertain the relation of the radicles to one another and, from the nature of the elements, deduce both the nature of the radicles and that of their compounds."

He then points out how the conception of the valency of the different elements may be utilised for this purpose. In this connection he further develops his ideas on the tetravalency of carbon, and gives the list of compounds:  $\text{CH}_4$ ,  $\text{CCl}_4$ ,  $\text{CH}_3\text{Cl}$ ,  $\text{CHCl}_3$ ,  $\text{COCl}_2$ ,  $\text{CO}_2$ ,  $\text{CS}_2$ ,  $\text{CNH}$ , pointing out that "the sum of the chemical units combined with one atom of carbon is 4. This leads to the view that carbon is *tetratomic* (or *tetrabasic*)."<sup>1</sup> At this point he introduces (*loc. cit.*, p. 153, footnote) a passing reference to the advantage of referring compounds to the marsh gas type: "If carbon is introduced as a *tetratomic radicle* among the types, several already known compounds may be formulated in a relatively simple manner."

He next proceeds to discuss the question of the linking of carbon atoms with one another:

"In the case of substances which contain several atoms of carbon, one must assume that some at least of the atoms are held in the compound in the same way [as in the cases already quoted] by the affinity of the carbon, and that the carbon atoms themselves are attached together, whereby a portion of the affinity of the one carbon atom is of course held in combination by an equal portion of the affinity of the other.

"The simplest and therefore most probable case of this union of two carbon atoms is that in which one unit of affinity of the one carbon atom is combined

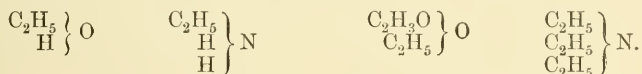


with one unit of affinity of the other. Of the  $2 \times 4$  units of affinity of the two carbon atoms, two are used up in holding the two atoms together; there therefore remain six which may be held in combination by atoms of other elements. In other words the group  $C_2$  is hexatomic. . . . .

"If more than two carbon atoms unite in the same way, the basicity of the carbon group will be increased by two units for each fresh carbon atom. Thus the number of hydrogen atoms (chemical units) which may be combined with  $n$  carbon atoms is expressed by

$$n(4-2)+2=2n+2.$$

". . . Up to this point we have assumed that all the atoms attaching themselves to carbon are held by the affinity of the carbon. It is equally conceivable, however, that in the case of polyatomic elements (O, N &c.) only a part of the affinity of these—for example, only one of the two units of affinity of the oxygen, or only one of the three units of the nitrogen—is attached to carbon; so that one of the two units of affinity of the oxygen, and two of the three units of affinity of the nitrogen, remain over and may be united with other elements. These other elements are therefore only in indirect union with the carbon, a fact which is indicated by the typical mode of writing the formulæ:



"In like manner the carbon groups are held together by the oxygen or the nitrogen."\*

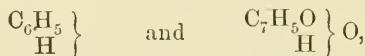
He points out that a great many organic compounds may be formulated on the basis of the "simplest" attachment of carbon to carbon, but that, in others which contain more carbon in proportion the "next simplest" attachment may be assumed, involving a closer union of the carbon atoms. He does not, however, go into details regarding the principles to be adopted in formulating such unsaturated compounds.

It is to be noted that at that time Kekulé still held Gerhardt's view that rational formulæ were merely an expression of chemical reactions. The idea that it was possible to express the relative positions of the atoms within the molecule was of later growth.

Kekulé had by his interpretation of the types in terms of the law of valency, and by his dissection of the compound radicles in accordance with the same law, superseded both the type theory and the radicle

\* As a further example of how little Kolbe thought it necessary to master the details of theories he set himself to criticise, the following passage may be quoted, in which, after making merry over the expression "carbon skeleton," used by Kekulé in the foregoing paper, he says (*J. pr. Chem.*, 1881, [ii], 24, 407): "If I am not mistaken, it is assumed that *all* organic compounds which contain more than one atom of carbon possess such carbon skeletons. Where, then are we to place the cacodyl compounds, trimethylamine, trimethylsulphine iodide and other organic substances?"

theory, except so far as they might be useful for purposes of exposition. Nevertheless, partly as a concession to the prevailing usage of his school, and partly, doubtless, from force of habit, he continued for a long time to write typical formulæ. This led to a somewhat mechanical mode of formulation, occasionally attended with misleading results. Thus, in the paper just quoted (pp. 145—146), we find benzene formulated on the hydrogen type and benzoic acid on the water type,



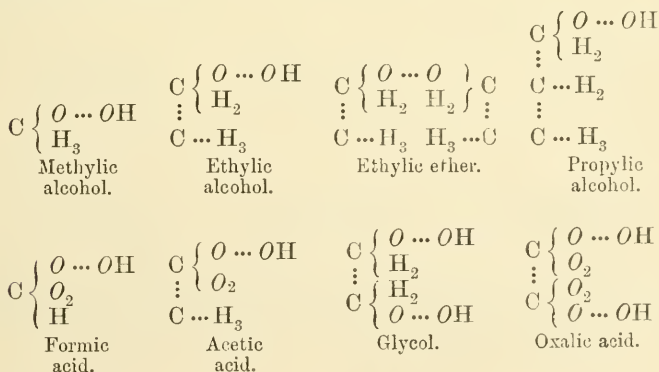
which leads him to state that, in the sulphonation of benzene, it is the typical hydrogen, but, in that of benzoic acid, hydrogen of the radicle, which is replaced, and to assign these reactions to two distinct categories. Again the hydroxy-acids are formulated on the double water type; thus lactic acid is  $\left. \begin{array}{c} \text{C}_3\text{H}_4\text{O}'' \\ \text{H}_2 \end{array} \right\} \text{O}_2$ ; a mode of representing these substances which obliterates the distinction between the acidic and the alcoholic hydrogen atoms, and was responsible for the errors into which Wurtz fell in the earlier part of his well-known controversy with Kolbe. Kekulé himself is perfectly clear about the difference between these two typical hydrogen atoms and explains its cause with all possible precision (*Lehrbuch*, 1, 731); nevertheless he quotes the formula  $\left. \begin{array}{c} \text{C}_3\text{H}_4(\text{HO})\text{O} \\ \text{H} \end{array} \right\} \text{O}$  for lactic acid (first put forward in the old equivalents by Kolbe) only to reject it with the remark (*loc. cit.*, p. 736): "Such formulæ offer no advantages over the typical formulæ; on the contrary they conceal a great number of analogies and, in other cases, cause analogies to be suspected where none exist." I venture to think that I have just shown that the typical formulæ are not quite free from these defects. As regards the particular case of the formula of lactic acid, there is no doubt that the reluctance which Kekulé and his school at that time displayed to make use of the hydroxyl group in formulating compounds was an effect of Laurent's supposed burlesque proof of the existence of the radicle *eurhyzene*, that is, hydroxyl (see Laurent's *Chemical Method*, Odling's translation, p. 293). I say "supposed burlesque," because, at the present day, there is probably no chemist who has occasion to refer to "the hydroxyl-group"—which, in chemical compounds, is an abstraction and, in certain electrolytic dissociations, an entity—but would willingly subscribe, in all seriousness, the words which Laurent wrote in jest.\*

\* When, however, Kekulé (*Lehrbuch*, 1, 736, footnote) quotes Laurent's *eurhyzene* as a proof that Kolbe's view of the constitution of the acids of the lactic series as hydroxy-derivatives of the acids of the acetic series, is not original, one can only surmise that he was infected by Laurent's spirit of elaborate pleasantry.

This adherence to the outward form of the typical formulæ was, however, a minor defect, especially as Kekulé showed in his *Lehrbuch* how, by means of his graphic formulæ, the relations of the different atoms to one another within the molecule might be clearly exhibited. The graphic symbols were, however, as Kekulé himself pointed out, too cumbrous for ordinary use; they shared the fate of Dalton's atomic symbols and had to yield to the superior simplicity of those of Berzelius, which, with a few additions in the shape of bonds and valency marks, were found to satisfy all requirements. Even the circles with which Crum Brown, in his system of graphic formulæ, at first surrounded the symbols, were soon discarded.

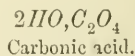
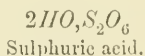
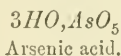
Kekulé's models of atoms, on the other hand, to which reference will be made later, had a brilliant future before them.

It must be mentioned that, shortly after the publication of Kekulé's paper on the constitution of chemical compounds, analogous views were put forward independently by Couper (*Ann. Chim. Phys.*, 1858, [iii], 53, 469; *Phil. Mag.*, 1858, [iv], 16, 104). The two investigators followed different paths, and their results were in some respects different. Kekulé accepted the type theory and furnished it with a philosophical basis by explaining the existence of the pattern formulæ, or types—simple, multiple, and mixed—by means of the valency of the constituent elements; Couper, on the other hand, rejected the type theory altogether, and, starting with the idea of the valency of the elements, proceeded to construct constitutional formulæ for various compounds. Couper held peculiar views on the subject of the atomic weights: thus, whilst carbon was  $C = 12$ , oxygen was only  $O = 8$ . Carbon was tetradic; and the small oxygen atoms were dyadic, but were supposed always to occur linked together in pairs, so that the resulting group,  $O \dots O$ , as Couper wrote it, was also dyadic, and was therefore, to all intents and purposes, identical with the dyadic  $O = 16$ . The following formulæ will illustrate his system:

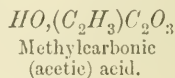
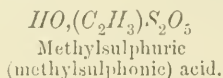
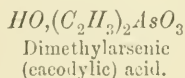


Couper's formulæ are thus, in spite of the peculiarity in the mode of writing oxygen, nearer to our present formulæ than those used by Kekulé at that period, and from the manner in which he discusses them it is evident that he intends them to be constitutional formulæ and not mere "formulæ of double decomposition" such as were employed by Gerhardt's school. The constitution assigned to the foregoing compounds is, however, identical with that previously proposed by Kolbe, with a difference, however, in the mode of writing the formulæ.

Kolbe (*J. pr. Chem.*, 1881, [ii], 23, 366) and Frankland (*Proc. Roy. Soc.*, 1865, 14, 198) claim to have anticipated Kekulé's enunciation of the tetravalency of carbon in a paper which they \* published in 1857 (*Annalen*, 1857, 101, 262 *seq.*). This claim, however, cannot be sustained, unless we ignore the list of compounds formulated on the marsh gas type, which Kekulé drew up in his paper on mercuric fulminate published a short time previously. Kolbe, indeed, gave what he considered to be reasons for ignoring this list; but I believe I have shown (p. 123) that these supposed reasons are based on a misunderstanding of Kekulé's meaning. Kolbe and Frankland's paper appeared so soon after Kekulé's that there can be no doubt of their having arrived at their conclusions quite independently of Kekulé, the more so as these conclusions are drawn entirely from their own work. Moreover, as the whole paper deals with the application of the law of valency, discovered by Frankland, to the interpretation of the constitution of organic compounds, it is clear that the authors had the tetravalency of carbon, or rather the tetravalency of the double equivalent,  $C_2$ , in their minds, although they did not mention it in so many words. Frankland had already shown (*v. supra*) how cacodylic acid might be derived from arsenic acid, or, strictly speaking, how the hypothetical cacodylic anhydride might be derived from arsenic anhydride, by replacing two equivalents of oxygen by two of methyl. Kolbe and Frankland now apply this view to the hydrated acids: thus from



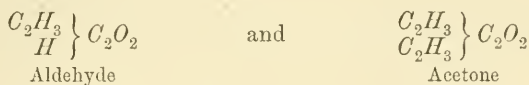
they deduce




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\* Through inadvertence this paper appeared under Kolbe's name only (compare Frankland's *Experimental Researches*, p. 148). Except in the opening sentences, in which Kolbe is referring to previous work of his own, the pronoun "we" is used throughout as denoting the joint authors.

They point out that, for each atom (equivalent) of oxygen which is replaced by methyl, one equivalent of water  $HIO$  is simultaneously removed, so that for each introduction of a methyl group the basicity of the acid is reduced by 1. By replacing a further atom (equivalent) of oxygen in acetic acid by hydrogen or by methyl and again simultaneously removing  $HIO$ , they obtain



which are no longer acids at all. Further on, in the same paper, they point out that carbonic acid may be formulated  $2HO, (C_2O_2)O_2$ , and that it is the two "extra-radical" oxygen atoms which are replaced by methyl, each carrying with it an equivalent of water.

If we translate this into modern atomic weights, each "extra-radical" equivalent of oxygen, plus an equivalent of water, represents a hydroxyl group:  $O + HO(O = 8) = OH(O = 16)$ ; so that the above formula for carbonic acid is identical with  $CO(OH)_2$ . It is thus hydroxyl of the hypothetical carbonic acid, and not, as the authors suppose, oxygen of carbonic anhydride, which is replaced by methyl or hydrogen in the foregoing mode of deducing acetic acid, aldehyde, and acetone from carbonic acid.

The tetravalency of the double equivalent of carbon,  $C_2$ , is certainly implied in Kolbe and Frankland's paper; but, as already mentioned, it is nowhere expressly stated, and one may be permitted to doubt whether many chemists could at that period have disentangled the doctrine from the very complicated hypothesis in which the use of the old equivalents had compelled the authors to involve it. Those who profited most by the work were those who could translate it into Gerhardt's atomic weights, and probably Kekulé and his school were more indebted to it than they were at that time conscious of. It is clear, however, that the paper contains no hint of the linking of carbon atoms, as this conception could not be developed in terms of Gmelin's equivalents. Indeed, so far as Kolbe was concerned, even after he had accepted the new atomic weights, he continued, to the end of his life, to cast ridicule on this conception (compare *J. pr. Chem.*, 1881, [ii], 24, 414).

That Kolbe and Frankland's work on the tetravalency of carbon did not, therefore, exercise a direct and immediate influence in any degree comparable with that produced by Kekulé's great paper on the same subject, is to be ascribed to the fact that their conclusions were stated in terms of an inconsistent scheme of atomic weights. We must not forget, however, that the same principle, namely, that of the



derivation of organic acids, aldehydes and ketones from carbonic acid, led Kolbe, later on, to the prognosis of secondary and tertiary alcohols, of which triumph of theoretical foresight the germ is contained in the concluding paragraph of Kolbe and Frankland's paper (compare *Annalen*, 1857, 101, 265).

I have already referred to Kekulé's models of atoms. The conception which he introduced in these, as to the distribution of the four affinities of the carbon atom, has led to most important results. He begins by referring (*Zeitschr. f. Chem.*, 1867, *N.F.*, 3, 217) to the imperfections of his original system of graphic formulæ and of the models based upon them, and further points out that models constructed on the basis of Crum Brown's graphic formulæ and consisting of spheres with rods radiating from them in one plane, do not really express more than the graphic formulæ themselves, inasmuch as the representation which they afford of a space formula is only apparent, the atoms being all in the same plane; and that, unless the rods are bent or arbitrarily displaced, certain combinations, *e.g.* triple bonds between carbon atoms, cannot be represented by them at all. He then proceeds to describe a model of the carbon atom which he has devised and which avoids these difficulties: "The four units of affinity of the carbon atom, instead of being placed in one plane, radiate from the sphere representing the atom in the direction of hexahedral axes, so that they end in the faces of a tetrahedron. . . . A model of this description permits of the union of 1, 2 and 3 units of affinity, and, it seems to me, does all that a model can do."

Even while making this apparently sweeping statement, Kekulé can hardly have realised the part that this model was destined to play in the development of theoretical chemistry; how in van't Hoff's hands it was to be the means of tracing the subtle asymmetry which Pasteur had deduced from the optical behaviour and the crystalline form of certain organic compounds, back to the asymmetric structure of the molecule itself; of explaining the mysterious isomerism of fumaric and maleic acid, which had baffled Kekulé's own acumen; and of laying down the space conditions of existence or non-existence of the closed-chain compounds of which Kekulé himself had introduced the conception into chemistry in his benzene theory.

I have already referred to Kekulé's benzene theory as the crowning achievement of the doctrine of the linking of atoms. To give a complete account of this theory and of the criticisms to which it has been subjected, would far exceed the scope of the present lecture; whilst to treat it briefly may seem superfluous, as the theory, in its main outlines, is familiar to every one with even the most elementary knowledge of organic chemistry.

This theory was first published in 1865 in the *Bulletin de la Soc. Chimique* (1, 98). I quote, however, from the fuller account published a year later in Liebig's *Annalen* (1866, 137, 129).

In this paper, "On the Constitution of the Aromatic Compounds," Kekulé begins by stating that none of the chemists who have dealt with the subject of benzene and its derivatives, have attempted to deduce the constitution of these compounds from the tetravalency of carbon and that some have gone so far as to state that this cannot be done. He then enumerates various distinguishing characteristics of the benzene compounds: amongst others, that there is no benzene compound containing fewer than six carbon atoms. After pointing out that six carbon atoms might be linked together by alternate single and double bonds, he says:

"If one assumes that six carbon atoms are attached to one another according to this law of symmetry, one obtains a group which, regarded as an *open chain*, contains *eight* unsaturated units of affinity. By making the further assumption that the two carbon atoms at the ends of the chain are linked together by one unit of affinity each, a *closed chain* (a symmetrical ring) is obtained, which still contains *six* unsaturated units of affinity.\*

"From this *closed chain* all the substances usually designated as 'aromatic compounds' are derived. . . .

"In all aromatic substances a common nucleus may be assumed: it is the closed chain  $C_6A_6$  (in which A denotes an unsaturated affinity).

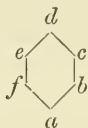
"The six affinities of this nucleus may be satisfied by six monatomic elements. They may also, wholly or at least in part, be satisfied by one affinity of polyatomic elements, the latter necessarily bringing with them other atoms into the compound, thus producing one or more *side chains*, which in their turn may be lengthened by the addition of other atoms.

"The satisfying of two affinities of the nucleus by one atom of a diatomic element, or of three affinities by one atom of a triatomic element, is, according to the theory, impossible. Compounds of the molecular formulæ,  $C_6H_4O$ ,  $C_6H_4S$ ,  $C_6H_3N$ , are, therefore, unthinkable."

Here we meet for the first time (if we except Kekulé's preliminary note on the same subject) with the now familiar expressions "closed chain," "nucleus," and "side chain," without which it would, at the present day, be impossible to discuss the problem of the constitution of the benzene compounds. The last paragraph quoted is worthy of note: it contains a very positive statement on a point which does not appear to follow with absolute necessity from the formulæ which Kekulé uses. It involves conceptions regarding the actual distribution of the atoms in space; and the conclusion at which Kekulé arrives suggests that he was already using the space-models of atoms which he described two years later.

\* In the original paper these atomic groups are represented by means of Kekulé's graphic formulæ.

He points out that the foregoing constitution of the benzene nucleus involves the equivalence of the six unsatisfied affinities and proceeds to deduce the number of possible substitution derivatives of benzene, containing 1, 2, 3, &c., identical substituents, the isomerism depending on the relative positions of the substituents towards one another. Amongst other things he points out that whereas there are only three substitution derivatives possible of the general formula  $C_6H_5X_3$ , there are six of the formula  $C_6H_3X_2Y$ . In stating this conclusion he makes use of a hexagon lettered as follows



and says: "For dibromnitrobenzene, for example, there would be the following forms:

- " (1) For  $a b c$  :  $C_6H_3BrBr(NO_2)$   
 $C_6H_3Br(NO_2)Br$   
 (2) For  $a b d$  :  $C_6H_2(NO_2)HBr_2$   
 $C_6H_2BrH(NO_2)Br$   
 $C_6H_2BrHBr(NO_2)$   
 (3) For  $a c e$  :  $C_6HBrHBr(NO_2).$ "

It was this series of compounds that Körner used later (*Gazzetta*, 1874, 4, 305) in his well-known method for the orientation of the bromine atoms in the dibromobenzenes.

The homologues of benzene are discussed. "The homology may depend either upon an increase in the number of the side chains, or on the lengthening of side chains the number of which remains the same." Thus there ought to be three dimethylbenzenes (only one was at that time known) and, isomeric with these, the synthetical ethylbenzene of Fittig and Tollens.

The law of oxidation of the homologues of benzene is laid down: namely, that each hydrocarbon side chain, no matter how many carbon atoms it may contain, is oxidised away, with the exception of the carbon atom attached to the nucleus, which remains in the shape of a carboxyl-group. The resulting acids thus contain as many carboxyl-groups as there were hydrocarbon side chains in the original compound. By more moderate oxidation intermediate products are obtained: thus, xylene and cymene both yield toluic acid. Moreover, the possibility is foreseen, in the case of side chains containing more than one carbon atom, of oxidising only a portion of the chain, and thus obtaining an acid in which the carboxyl is not directly attached to the nucleus.

The question of substitution in the nucleus and substitution in the

side chain is also gone into, and the difference in the character of the resulting derivatives is pointed out.

At the end of the theoretical portion of the memoir, Kekulé says, referring to different possible formulæ for benzene :

"A problem of this kind might at first sight appear quite insoluble ; but I nevertheless believe that experiment will furnish a solution. It is only necessary to prepare, by methods as varied as can be devised, as great a number of substitution products of benzene as possible ; to compare them very carefully with regard to isomerism ; to count the observed modifications ; and especially, to endeavour to trace the cause of their difference to their mode of formation. When all this is done we shall be in a position to solve the problem."

Could the course of subsequent investigation in this field have been more accurately laid down in advance ?

Kekulé's memoir on the benzene theory is the most brilliant piece of scientific prediction to be found in the whole range of organic chemistry. What Kekulé wrote in 1865 has since been verified in every essential particular. Not only have the various substitution derivatives been discovered, in the number and with the properties required by the theory, but various observations which appeared to contradict this theory have been proved erroneous. Moreover, the theory has shown itself capable of boundless development. There seems to be no limit to the fruitfulness of Kekulé's conception of closed chains or cycloids. The extensions of the idea, of which extensions Erlenmeyer's naphthalene formula and Dewar's formulæ for pyridine and quinoline were amongst the earliest instances, have gone on increasing in a rapid geometrical ratio, until, at the present day, the literature dealing with cycloids, although of so recent growth, is more than twice as voluminous as that of the paraffinoids. To quote the words of the address which our Society presented to Kekulé on the occasion of the *Benzolfeier* : "This theory found the chemistry of even the immediate derivatives of benzene an almost untilled field ; it has transformed it into a fertile province, to which have been annexed regions the very existence of which was unknown."

But even in the undeveloped state of the subject prior to Kekulé's theory, the facts were apparently so intricate and so unconnected that few chemists could claim to have mastered them. The theory appeared ; the previously unmarshalled facts fell into their proper places ; and not only this, but it was possible to say whether, in any given section of the subject, the facts were complete or only fragmentary. The increased ease in dealing with this branch of chemistry, the fascination of the numerous scientific problems which Kekulé's theory suggested, and lastly the economic importance of many of the benzene compounds and of other allied cycloids, attracted to this field

a crowd of workers, whose numbers, if they have not of late years actually increased, at least show no signs of diminishing. The debt which both chemical science and chemical industry owe to Kekulé's benzene theory is incalculable. As regards the former, three-fourths of modern organic chemistry is, directly or indirectly, the product of this theory; and as to the latter, the industries of the coal-tar colours and the artificial therapeutic agents, in their present form and extension, would be inconceivable without the inspiration and guidance which they have received and still receive from Kekulé's fertile idea.

Various points in Kekulé's theory which were at first either fundamental assumptions, or deductions from these fundamental assumptions, have since been experimentally proved: thus the equivalence of the six hydrogen atoms in benzene by Ladenburg, and the fact that there is, relatively to every hydrogen atom, a symmetrically situated ortho-pair and a symmetrically situated meta-pair, by Hübner and Petermann, Wroblewsky, and others.

The orientation of the substituents in the derivatives of benzene, merely indicated by Kekulé, has been successfully carried out by von Baeyer, Graebe, Ladenburg, Griess, and, above all, Körner. The concordant results obtained by the most diverse methods have placed this part of the subject on a sure foundation.

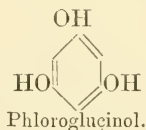
The non-identity of the two ortho-positions 1 : 2 and 1 : 6 in Kekulé's formula containing alternate double and single bonds, which is in contradiction to the proved identity of the two ortho-products and which would necessitate the existence of four isomeric disubstitution derivatives instead of three, has called forth much criticism. Kekulé sought to meet the difficulty by means of his well-known oscillation formula, in which the double and single bonds continually exchange places. This is virtually a return to the simple hexagon, given as an alternative formula by Kekulé in his original paper: the distribution of the unsaturated affinities is ignored.

Of the various formulae which have been proposed in place of Kekulé's, I will mention Ladenburg's prism formula, Claus's diagonal formula, and Armstrong and von Baeyer's central formula. All of these agree with Kekulé's formula in connecting together six CH-groups by single bonds so as to form a closed chain; the disposal of the remaining six affinities is the point wherein they differ. Ladenburg's formula is seldom discussed at the present day. It represents the ortho-carbon atoms as not directly connected, thus ignoring the analogy between the ortho-position in benzene compounds and the  $\alpha$ -position in paraffinoid compounds, and rendering the formulation of compounds like naphthalene and phenanthrene impossible, at least in accordance with the prevailing views. Moreover, the substitution of any two dissimilar groups for hydrogen would render carbon atoms of



the nucleus asymmetric, so that every compound of the general formula  $C_6H_4XY$  ought to exist in two enantiomorphous forms, whereas all efforts to isolate such forms have hitherto proved fruitless, benzene derivatives being optically inactive unless there is an asymmetric carbon atom in a side chain. Claus's diagonal formula was formerly objected to on the ground that the ortho- and para-positions were identical and that it therefore required the existence of only two di-substitution products. This difficulty has been got over by introducing spatial considerations and assuming that the greater distance between the para-carbon atoms, as compared with the ortho-, constitutes a difference. It is necessary, however, further to assume that the carbon and hydrogen atoms lie in one plane, otherwise asymmetric substitution derivatives would exist; and this assumption, taken in conjunction with that of para-bonds, would appear to demand the placing of the four affinities of carbon in one plane; in other words, it would involve the abandonment of van't Hoff's tetrahedron. The central formula is difficult to criticise; the mode of disposing of the central bonds is entirely without analogy and does not appear to be accessible to the test of experiment. In its application and predictions, the central formula is identical with Kekulé's simple hexagon.

The question of the disposal of these unsaturated affinities is, indeed, a very difficult one. Thus von Baeyer, who formerly opposed Claus's formula, has now, with certain limitations, adopted it (*Annalen*, 1892, 269, 177). According to him, it is impossible to devise a benzene formula which shall be applicable to all derivatives of benzene. He regards (*loc. cit.* p. 188) phthalic acid as derived from a benzene of Claus's formula and phloroglucinol from one of Kekulé's formula with alternate double and single bonds:



Possibly the solution of this difficulty will be found when we possess a space formula capable of representing these various modes of distributing the unsaturated affinities as different desmotropic oscillation-phases of a ring of 6 CH-groups (compare Collie, *Trans.*, 1897, 71, 1013). Of such a formula Kekulé's oscillation formula is a partial anticipation. Meanwhile chemists will doubtless continue to employ Kekulé's simple hexagon, without alternate double and single bonds, as a statical representation of the symmetry of the benzene molecule.

Various other important theoretical questions discussed by Kekulé might be mentioned here; but time does not permit.

If, in conclusion, we ask ourselves what is the characteristic note of Kekulé's theoretical creation, the chemistry of structure, I think we may reply that it is the treatment of the problem of isomerism—the problem which first necessitated the use of constitutional formulæ—as one of geometrical symmetry. Kekulé's formulæ, stripped of the fetters of the type theory with which he at first encumbered them, were, from one point of view, merely more or less symmetrical geometrical figures. In order to predict the number of substitution compounds, it was only necessary to consider the degree of dissymmetry of the parent compound: the less the symmetry, the greater the number of isomeric substitution compounds. The extraordinary fertility of this conception is shown by the development which it has undergone at the hands of van't Hoff, J. Wislicenus, von Baeyer, and others.

Kekulé's structural formulæ cleared away at one stroke the entire brood of pseudo-constitutional formulæ. If organic chemists no longer waste their time in wrangling over the question whether, for example, methylamine is methane in which one atom of hydrogen is replaced by the amido-group, or ammonia in which one atom of hydrogen is replaced by methyl, the merit is Kekulé's.

The accuracy of Kekulé's predictions has done more to inspire a belief in the utility of legitimate hypotheses in chemistry, and has therefore done more for the deductive side of the science, than that of almost any other investigator. His work stands pre-eminent as an example of the power of ideas. A formula, consisting of a few chemical symbols jotted down on paper and joined together by lines, has, as we have just seen, supplied work and inspiration for scientific organic chemists during an entire generation, and affords guidance to the most complex industry the world has yet seen.

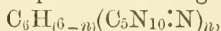
Although much research remains to be done on the lines laid down by Kekulé, yet other problems are clamouring for solution, and other methods of investigation have been called into existence to solve them. The younger generation of chemists are, fortunately, labouring diligently in the field of physico-chemical research, which the organic chemists, occupied with questions of chemical structure, had perhaps unduly neglected. One problem, however, which, in many points at least, still awaits the physical chemist, is the correlation of his results with those of the structural chemist. When this is fully accomplished, there will be a debt of gratitude on both sides; but no one will be entitled to more gratitude than August Kekulé.

VI.—*Compounds of Piperidine with Phenols.*

By OTTO ROSENHEIM, Ph.D., and PHILIP SCHIDROWITZ, Ph.D.

## INTRODUCTORY.

THE action of piperidine on dihydric and trihydric phenols and their derivatives in the presence of dehydrating agents was studied with the object of obtaining compounds of the general formula



as such substances, on account of their relation to the phenylene-diamines and the polyamines, would be of interest. Our experiments in this direction have not as yet led to the desired result, but, instead, a series of additive products was obtained, and as these have not hitherto been described \* we propose to give some account of them in this paper.

As a rule, they can be obtained well crystallised and practically pure by mixing solutions in ether or light petroleum of the base and the phenol.

Their behaviour towards strong acids and alkalis, by which they are at once resolved into their components, is evidence of the labile, additive character of the salts. With the exception of the yellow nitro-derivatives, they are all colourless, and, as a rule, easily soluble in water and most organic solvents. After a time, and in some cases almost instantaneously, the aqueous solutions undergo characteristic colour changes (compare Oechsner de Coninck, *loc. cit.*), possibly due to the formation of more complicated substances, in which the piperidine radicle is directly united to the benzene ring. This change was studied more minutely in the case of the quinol derivative, the colouring matter formed being well crystallised and easily isolated.

The analysis of these substances and their behaviour towards acids lead us to the conclusion that they are of the nature of salts in which piperidine is the basic, and the phenol the acid constituent.†

Phenol and  $\alpha$ - and  $\beta$ -naphthol do not yield crystallisable compounds.‡

\* Oechsner de Coninck (*Compt. rend.*, 1897, 124, 563), in a paper entitled "Action du tannin et d'autres dérivés aromatiques sur quelques alcaloïdes et urées composées," describes various colour reactions obtained by the action of piperidine on phenols in dilute aqueous solutions, but apparently did not observe the formation of the primary additive products.

† Substances of a similar nature were obtained by the action of phenols on aniline (A. Hebebrandt, *Ber.*, 1882, 15, 1973; F. Mylius, *Ber.*, 1886, 19, 1002), and piperazine (Schmidt u. Wichmann, *Ber.*, 1891, 24, 3237).

‡ T. Abel (*Ber.*, 1895, 28, 3106) only obtained a very small quantity of *o*-phenyl-piperidine, when operating with phenol and piperidine in sealed tubes at high temperatures, but found that  $\alpha$ - and  $\beta$ -naphthol reacted easily.

There is apparently no direct connection between the number of piperidine molecules uniting with the phenol and the number of hydroxy- or other radicles of an acid nature contained in the latter; but the *position* of the negative group appears to be of importance:

(1.) *In regard to the formation of the compounds.*—The meta-position appears to be the most unfavourable. Resorcinol,\* phloroglucinol, and metanitrophenol do not yield crystallisable compounds, whereas pyrocatechol, quinol, 1 : 2 : 4- $\alpha$ -dinitronaphthol, ortho- and para-nitrophenol, guaiacol, picric acid, &c., do so with ease.

(2.) *In regard to molecular combining proportions.*—The influence of position is apparently of a more complex nature, and the most noticeable feature is rather the lack of influence of the number of negative groups, more especially of the hydroxyl-group, in the acid constituent. Thus 1 mol. of piperidine combines with 1 mol. of quinol (2 hydroxyls), 1 mol. of pyrogallol (3 hydroxyls), 1 mol. of vanillin, and 1 mol. of ortho- or para-nitrophenol; but with 2 mols. of pyrocatechol and 2 mols. of pyrocatechol monomethyl ether. It may be added here that, in all cases, variation in the proportions of the substances employed has no effect on the composition of the final product.

#### EXPERIMENTAL.

In the majority of cases, the method of obtaining these substances was broadly as described under piperidine-pyrocatechol. Any distinct variation will be noted in the proper place. The yield is in almost every instance quantitative.

#### *Piperidine-Pyrocatechol*, $C_5H_{11}N.(C_6H_6O_2)_2$ .

Cold concentrated ethereal solutions of pyrocatechol (2 mols.) and piperidine (1 mol.), when mixed, began to boil owing to the violence of the action, and the salt separated almost immediately in glistening scales, which were at once collected, washed with a little ether, and rapidly dried in a vacuum. The white crystals thus obtained, as also the ethereal solution (if not anhydrous), quickly assume a reddish tint, and finally become brown on exposure to the air. If aqueous solutions of piperidine and pyrocatechol are mixed, using the former in excess, the liquid remains clear, but rapidly becomes wine red and finally dark brown. If excess of pyrocatechol is employed, however, the salt described above is precipitated as an oil, which solidifies on rubbing it with a glass rod.

\* F. Mylius (*Ber.*, 1886, 19, 1002) failed to obtain an additive product from aniline and resorcinol, but succeeded in the case of pyrocatechol.

The substance melts at 80—81°, and is very soluble in water and most organic solvents, with the exception of light petroleum.

Found, C = 67.10 ; H = 7.52 ; N\* = 4.87 per cent.

$C_{17}H_{23}O_4N$  requires C = 66.85 ; H = 7.59 ; N = 4.60 per cent.

*Piperidine-Guaiacol*,  $C_5H_{11}N, [C_6H_4(OCH_3)(OH)]_2$ ,

is best obtained by dissolving the guaiacol (2 mols.) in benzene and the piperidine (1 mol.) in light petroleum, and after thoroughly washing the white, crystalline mass with light petroleum, recrystallising from acetone or a mixture of benzene and light petroleum. It forms splendid colourless prisms, melting at 79—80°, and fairly soluble in water, very easily in benzene, alcohol, ether, acetone, and ethylic acetate, but almost insoluble in light petroleum. The pure substance gradually assumes the odour of guaiacol on exposure to the air.

Found, C = 69.02 ; H = 8.21 ; N = 4.32 and 4.41 per cent.

$C_{19}H_{27}NO_4$  requires C = 68.42 ; H = 8.16 ; N = 4.21 per cent.

The substance, when evaporated several times on the water bath with concentrated hydrochloric acid, is totally decomposed, the whole of the guaiacol being volatilised and piperidine remaining as hydrochloride. In a quantitative experiment, this was dried and weighed. Found, 36.6 per cent.; calculated for weight of piperidine hydrochloride, 36.5 per cent. Under similar conditions, pyrocatechol monethyl ether gives no crystallised salt.

We are indebted to Dr. F. W. Tunncliffe for the physiological and therapeutical examination of this product, and a short note on this subject, which he has sent us, will be found at the end of this paper.

*Piperidine-Quinol*,  $C_5H_{11}N, C_6H_6O_2$ .

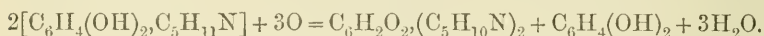
This was obtained from the ethereal solution (1 mol. of each) of the components in a pure state as colourless nodules made up of small needles; on heating, it turns brown, and finally melts at 102—104°. The white crystals gradually become reddish, and finally deep purple on exposure to the air, even when kept in a stoppered bottle, Lachowitz's dipiperilbenzoquinone being no doubt formed (*Monatsh.*, 1888, 9, 506). This transformation proceeds with great rapidity in an alcoholic solution of the salt, which, after 24 hours, becomes deep purple and deposits dark blue crystals. These were easily

\* Nitrogen was throughout estimated by Dumas' method. We found that Gunning's modification of Kjeldahl's method (*Zeitschr. f. anal. Chem.*, 1889, 28, 189), which has always given us admirable results in the analysis of food stuffs, &c., invariably yielded several per cent. too little in the case of the substances described in the present paper.



identified by their melting point,  $178^{\circ}$ , and their insolubility in water and organic solvents, with the product obtained by Lachowitz mentioned above. This change, however, does not take place if the salt is kept in a sealed tube, even when exposed for several months to strong sunlight.

The transformation of the white additive product into the blue substance which, according to Lachowitz, contains the piperidine radicle directly united to the benzene ring, appears to be due to the action of oxygen,



The fact that Lachowitz worked with an alcoholic solution in which piperidine-quinol is easily soluble, is no doubt the reason why he failed to observe the formation of the intermediate product.

Found, C = 67.52 and 67.96; H = 8.66 and 8.69; N = 7.27 per cent.

$\text{C}_{11}\text{H}_{17}\text{NO}_2$  requires C = 67.61; H = 8.77; N = 7.19 per cent.

When resorcinol or phloroglucinol were treated with piperidine under similar conditions, a thick, resinous mass was obtained, from which no crystalline product could be isolated.

*Piperidine-Pyrogallol*,  $\text{C}_5\text{H}_{11}\text{N}, \text{C}_6\text{H}_6\text{O}_3$ .

This is obtained in white needles, which evolve gas at  $110^{\circ}$ , become discoloured at  $140^{\circ}$ , and melt at  $171^{\circ}$ ; it is easily soluble in water and alcohol, but almost insoluble in benzene, chloroform, acetone, and ethylic acetate. The aqueous and alcoholic solutions of the salt rapidly change colour, passing through yellow to a dirty brown.

Found, N = 6.60 and 6.57 per cent.

$\text{C}_{11}\text{H}_{17}\text{NO}_3$  requires N = 6.63 per cent.

*Piperidine-Vanillin*,  $\text{C}_5\text{H}_{11}\text{N}, \text{OH} \cdot \text{C}_6\text{H}_3(\text{OCH}_3) \cdot \text{COH}$ .

This separates from the ethereal solution as an oil which is converted into a crystalline mass on rubbing it with a glass rod. When recrystallised from ethylic acetate, it is obtained in well-defined, colourless crystals melting at  $70^{\circ}$ ; it is soluble in water, alcohol, and benzene, but almost insoluble in ether and light petroleum. When kept, it is gradually transformed into a dark-red, resinous mass smelling strongly of vanillin; the alcoholic and aqueous solutions of the salt show the same change of colour.

Found, N = 5.63 per cent.

$\text{C}_{13}\text{H}_{19}\text{NO}_3$  requires N = 5.90 per cent.

*Salts of the Nitrophenols.\***Piperidine-Paranitrophenol*,  $C_5H_{11}N, C_6H_4(NO_2) \cdot OH$ .

This is formed from its components in molecular proportion dissolved in ether. When recrystallised from acetone, it forms large, lemon-yellow rhombohedrons about 1 cm. in length; it melts at  $110^\circ$ , and is easily soluble in water, alcohol, or chloroform, less readily in ether, and almost insoluble in light petroleum. It is at once decomposed by alkalis and by acids even in dilute solution, the disappearance of the yellow colour on adding acids to an aqueous solution indicating the point of saturation. Taking advantage of this, it was found that 0.1206 gram required 5.25 c.c. N/10 hydrochloric acid. Calculated 5.30 c.c.

A nitrogen determination gave  $N = 12.87$  per cent., whilst  $C_{11}H_{16}N_2O_3$  requires  $N = 12.54$  per cent.

*Piperidine-Orthonitrophenol*,  $C_5H_{11}N, C_6H_4(NO_2) \cdot OH$ .

In adding a solution of orthonitrophenol (1 mol.) in benzene to piperidine (1 mol.) diluted with light petroleum, the colour of the solution changes to a brilliant orange and an oil of the same colour is deposited; the latter rapidly solidifies to a crystalline mass on adding a small crystal of the salt (accidentally obtained by evaporating a few drops of the solution on the water-bath). After recrystallisation from a mixture of benzene and light petroleum, it was obtained in stellate clusters of slender orange prisms, melting at  $83-84^\circ$ ; it is easily soluble in water, alcohol, ether, and most organic solvents. The aqueous solution is decomposed on boiling, yellow vapours of orthonitrophenol being given off.

Found,  $N = 12.66$  per cent.

$C_{11}H_{16}N_2O_3$  requires  $N = 12.50$  per cent.

0.1884 gram (standardised as described under paranitrophenol, piperidine) required 8.3 c.c. N/10 hydrochloric acid. Calculated 8.4 c.c.

*Piperidine-Picrate*,  $C_5H_{11}N, C_6H_2(NO_2)_3 \cdot OH$ .

This substance has been mentioned in literature, but not described, and as it may be of use for the identification of piperidine, we think it of interest to give a short description of its properties. On

\* T. Abel (*Ber.*, 1895, **28**, 3106) examined the action of piperidine on mononitrophenols at higher temperatures, with the object of obtaining nitrophenol-piperidines, but does not seem to have observed the formation of intermediate products.

adding piperidine (1 mol.) diluted with a little ether to trinitrophenol (1 mol.) dissolved in equal parts of alcohol and ether, the mixture became warm; on cooling, the picrate crystallised out in brilliant yellow needles, which, after recrystallisation from water or alcohol, melted at  $145^{\circ}$  (but were partially decomposed at  $112^{\circ}$ ). It is sparingly soluble in cold, easily in hot water, and melts under boiling water to a yellow oil; it is easily soluble in acetone or ethylic acetate, but nearly insoluble in benzene and light petroleum.

Found, N = 18.07 per cent.

$C_{11}H_{14}N_4O_7$  requires N = 17.88 per cent.

Neither  $\alpha$ - nor  $\beta$ -naphthol forms salts with piperidine, a fact which is somewhat surprising, when we take into account the ease with which piperidine reacts with naphthols at higher temperatures to form naphthylpiperidines (T. Abel, *Ber.*, 1895, 28, 3106). On the other hand, 1:2:4-dinitronaphthol forms an additive product with the greatest ease.

*Piperidine-Dinitronaphthol*, [1 : 2 : 4]  $C_5H_{11}N, C_{10}H_5(NO_2)_2 \cdot OH$ .

This is obtained by mixing solutions of piperidine and dinitronaphthol (in light petroleum and benzene respectively) in molecular proportion; after recrystallising from alcohol, it is obtained in orange needles melting at  $205^{\circ}$ . It is easily soluble in water and hot alcohol, but only very sparingly in ether and benzene.

Found, N = 13.44 per cent.

$C_{15}H_{17}N_3O_5$  requires N = 13.16 per cent.

*Tannin*, when treated with piperidine in ethereal solution, yields a substance which becomes resinous and undergoes further changes so rapidly that we refrained from analysing it (see Oechsner de Couinck, *loc. cit.*). *Gallic acid*, like other acids, yields a salt; it melts at  $206$ — $207^{\circ}$  and decomposes at  $210^{\circ}$ .

We propose to examine the action of other secondary bases on phenols under similar conditions, and may add that, from our preliminary experiments, tertiary bases do not seem to yield additive compounds. As a curious fact, however, we may mention that, although pyridine does not react with phenols, quinoline, in ethereal solution, forms a well crystallised product (m. p.  $94$ — $95^{\circ}$ ) with quinol.

*Note on the Physiological Action of Guaiacolate  
of Piperidine.*

By F. W. TUNNICLIFFE, M.D., M.R.C.P.

This substance has already been introduced into medicine, and has been found to be of considerable service in phthisis. It forms a relatively soluble salt, and can be given either in solution or in the solid form. It has none of the irritant properties of guaiacol, and there is every reason to believe that the base, that is, the piperidine, not only neutralises these irritant properties but exerts its own specific action, namely, that of a vascular and nervine tonic. The importance of a vascular tonic in the treatment of the infective granulomata (tuberculosis) has recently been emphasised by Liebreich, who has found, both in the treatment of pulmonary tuberculosis and lupus, cantharidine to be of great service; the principal action of this substance is attributed by Liebreich almost entirely to its vascular tonic action. The combination, therefore, of a vascular tonic, one of the strongest known (perhaps the strongest with the exception of nicotine), and an antiseptic like guaiacol must be regarded pharmacologically as an advance, and the practical results obtained with this substance, although at present few, seem to prognosticate for it a distinct place amongst the remedies for consumption.

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*VII.—Action of Chloroform and Alkali Hydroxides  
on the Nitrobenzoic Acids.*

By WALTER J. ELLIOTT, M.A.

IN a former communication (Trans., 1896, 69, 1513), it was shown that potassium hydroxide in aqueous solution and chloroform, by their conjoint action on metamidobenzoic acid, produced a substance allied to the aldehydes. The action of these agents on other substituted benzoic acids is now being investigated, this communication dealing with their action on the nitro-acids.

As in the previous research the amido-group had not been attacked, it was thought that the nitro-group would also remain unchanged but this has not proved to be the case. When the attempt was made to bring about a change under the conditions obtaining in the case of the

amido-acid, no action occurred; however, on varying the proportions and the time, products were eventually obtained from the meta- and para-acids which proved to be products of reduction, azoxy-acids, in fact. No compound was formed from the ortho-acid, although some slight action apparently takes place. The yield in every case is small.

*Preparation of Metazoxybenzoic Acid.*

After many trials, the following method was found to give the best yield. Both potassium hydroxide and sodium hydroxide were used, but no difference in their action could be detected.

To 10 grams of metanitrobenzoic acid dissolved in a solution of 40 grams of sodium hydroxide in 250 c.c. of water, 30 grams of chloroform were added, and the whole heated by a small flame for 6 hours in a flask fitted with a reflux condenser. The solution, after being filtered, diluted, and acidified with dilute sulphuric acid, was boiled, and again filtered; the filtrate contains the greater part of the unaltered nitro-acid, which can be easily recovered by crystallisation; the crystals had the melting point of the nitro-acid ( $141^{\circ}$ ), and, on analysis, gave numbers corresponding with 8.37 per cent. of nitrogen. The precipitate, after being well washed with boiling water to remove the rest of the nitro-acid, was boiled with alcohol, which removed the last traces, filtered, and washed with hot alcohol. As the residue was only slightly soluble in alcohol and insoluble in water, it was purified by dissolving it in dilute ammonia and precipitating with dilute sulphuric acid; after washing with hot water and hot alcohol and drying at  $100^{\circ}$ , a product was obtained which gave concordant results on analysis.

The purified product is a yellowish powder slightly soluble in alcohol, from which it separates as a crystalline powder, slightly soluble in ether, insoluble in water. It does not melt below  $300^{\circ}$ , but becomes darker in colour above  $250^{\circ}$ .

The following numbers were obtained on analysis.

- I. 0.1703 gave 0.0556  $\text{H}_2\text{O}$  and 0.3658  $\text{CO}_2$ . C = 58.58; H = 3.62.
  - II. 0.1892 „ 0.0603  $\text{H}_2\text{O}$  „ 0.4082  $\text{CO}_2$ . C = 58.83; H = 3.54.
  - III. 0.1806 „ 15.6 c.c. moist nitrogen at  $17^{\circ}$  and 760.6 mm. N = 9.96.
  - IV. 0.1651 „ 14.2 c.c. moist nitrogen at  $16^{\circ}$  and 762.6 mm. N = 9.94.
- $\text{C}_{14}\text{H}_{10}\text{N}_2\text{O}_5$  requires C = 58.74. H = 3.49; N = 9.79 per cent.

It is therefore metazoxybenzoic acid. This acid was prepared by Griess (*Annalen*, 1864, 131, 92) by the action of alcoholic potash on metanitrobenzoic acid. A specimen prepared by Griess's method was found to have properties similar to those of the acid described above.

The silver salt was obtained as a flocculent, faintly-yellow pre-



precipitate on adding silver nitrate solution to a neutral solution of the ammonium salt; it is slightly soluble in boiling water, and separates as a flocculent precipitate which is very stable in air, and is not affected by light at the ordinary temperature. The silver salt, dried at  $100^{\circ}$ , was analysed.

I. 0.1460 gave 0.0626 Ag. Ag = 42.87.

II. 0.2754 „ 0.1182 Ag. Ag = 42.91.

$C_{14}H_8N_2O_5Ag_2$  requires Ag = 43.2 per cent.

The barium salt, obtained as a yellow, crystalline precipitate on adding barium chloride solution to a neutral solution of the ammonium salt, is almost insoluble in water, and was purified by repeated washing with boiling water; the crystals are in the form of minute plates. The salt was dried at  $120^{\circ}$  and analysed.

I. 0.4385 gave 0.2419  $BaSO_4$ . Ba = 32.43.

II. 0.5367 „ 0.2953  $BaSO_4$ . Ba = 32.35.

$C_{14}H_8N_2O_5Ba$  requires Ba = 32.54 per cent.

#### *Preparation of Parazoxybenzoic Acid.*

This acid was obtained and purified by the methods used in the case of the meta-acid. It is a bright yellow, amorphous powder, insoluble in all solvents; it does not melt, but becomes darker in colour when heated to a high temperature. The purified acid, dried at  $100^{\circ}$ , gave the following numbers on analysis.

0.1933 gave 0.0636  $H_2O$  and 0.4148  $CO_2$ . C = 58.52; H = 3.65.

0.2504 „ 22 c.c. moist nitrogen at  $17^{\circ}$  and 759 mm. N = 10.06.

The silver and barium salts were obtained by the methods used for the preparation of similar salts of the meta-acid.

The silver salt is a bright yellow, amorphous substance, insoluble in water, and very stable in air. It was dried at  $100^{\circ}$  and analysed.

0.2315 gave 0.1002 Ag. Ag = 43.28.

0.4172 „ 0.1792 Ag. Ag = 42.95.

The barium salt is precipitated in minute, dark yellow plates insoluble in water. It was dried at  $120^{\circ}$  and analysed.

0.2928 gave 0.1617  $BaSO_4$ . Ba = 32.47.

After many trials with varying quantities of the interacting substances, nothing but the original nitro-acid was obtained from ortho-nitrobenzoic acid. Some slight action takes place, since there is considerable change of colour on prolonged heating, but all attempts to isolate a definite product have failed; from this it would seem that the nitro-

group in the ortho-position is less easily reduced than when it is in the meta- or para-position.

In the cases where the azoxy-acid is produced, there is brisk effervescence on acidifying the solution after boiling with chloroform, carbon dioxide being evolved in considerable quantity; this fact seems to show that the reduction of the nitro-group is accompanied by oxidation of the alkali formate to carbonate.

The investigation of the conjoint action of chloroform and alkali hydroxides on other substituted benzoic acids, such as the chlorinated acids and the ortho-amido-acid, is now being attempted, and I hope to communicate the results to the Society in a short time.

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BRISTOL.

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## VIII.—*New Method of Preparing Pure Iodine.*

By BEVAN LEAN, D.Sc., B.A., and W. H. WHATMOUGH.

### *Introduction.*

IN his *Nouvelles Recherches sur les Lois des Proportions Chimiques* (p. 136), Stas says:—

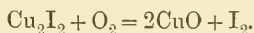
“ Pour effectuer une synthèse complète d’iodure d’argent, j’ai dû nécessairement me procurer d’abord de l’iode pur. Tous les moyens indiqués pour arriver à ce résultat ne m’ont point paru présenter des garanties suffisantes. Aucun de ces moyens, en effet, n’exclut la possibilité de la présence du chlore ni de brome. Après avoir mûrement examiné toutes les conditions dans lesquelles on peut probablement parvenir à obtenir de l’iode; je n’ai pu en découvrir que deux: l’une consiste dans la précipitation, par l’eau, de l’iode dissous dans une solution d’iodure de potassium; l’autre réside dans la décomposition de la diiodamine par la chaleur. En effet, le chlore et le brome, contenus dans l’iode employé, doivent rester unis soit au potassium, soit à l’ammonium. . . . Délayé dans de l’eau, l’iode a été introduit ensuite dans une grande cornue tubulée, et distillé à la vapeur d’eau pure. Cet iode après avoir été égoutté, a été exposé sous une cloche contenant de l’azotate de chaux desséché. L’azotate de chaux a été renouvelé tant qu’il s’est humecté. Ce sel de chaux a été la seule matière que j’ai pu découvrir pour sécher l’iode sans lui communiquer des impuretés.

“ L’iode, desséché aussi bien que possible, a été mêlé de cinq pour cent de son poids de protoxyde de baryum pur finement pulvérisé et soumis à la distillation sèche. Il a été reçu dans une cornue tubulée qui servait de récipient et qui contenait aussi du protoxyde de baryum pur finement pulvérisé; il a été rectifié une deuxième fois, en condensant sa vapeur dans une cornue vide. . . . En distillant l’iode sur du protoxyde de baryum, j’avais un double but: je voulais le priver de l’eau qu’il retient avec une grande opiniâtreté ainsi que l’acide iodhydrique. . . .

“L’iode, produit ainsi, diffère notablement, par son aspect, de celui du commerce. Après avoir été fondu dans un tube de verre, il est absolument noir à l’état liquide et solide : à la température ordinaire, il n’émet aucune vapeur visible dans l’air. . . . On admet généralement que le point de fusion de l’iode est 107°, et que son point d’ébullition est compris entre 175° et 180°. L’iode de la diiodamine est encore solide à 113° ; mais il est liquide à 115°, et ne bout pas encore à 200°.”

The chief difficulties which Stas had to overcome in the preparation of iodine were its separation from bromine and chlorine, and subsequently the removal of moisture and hydriodic acid. It would be of great interest to learn in detail how Stas assured himself that his ‘iodine’ was free from other halogens, and that calcium nitrate was the only desiccating agent which did not introduce impurities to the iodine. No further information on these points can, however, be gleaned from his published researches ; several of his laboratory note-books kept in the Solvay Institute at Brussels, and courteously lent to us by the Director, Dr. Paul Héger, have also been carefully examined with the same object, but without success.

A few months ago, we observed incidentally that no iodine was set free when cuprous iodide was heated, even till fused, in a current of carbonic anhydride, although, as is well known, iodine is readily evolved when cuprous iodide is heated in air to a moderate temperature. A few preliminary experiments showed that the action was probably represented by the equation

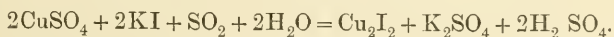


Now it has commonly been supposed that an iodide can be detected in the presence of other haloids by precipitation as cuprous iodide, and if so, it should be possible to prepare cuprous iodide free from bromide or chloride, and then from it liberate pure iodine in the way indicated above.

With the object of preparing iodine, free in particular from chlorine, bromine, hydriodic acid or water, the whole question was submitted to careful examination.

### *Preparation of Cuprous Iodide.*

*Action of Copper Sulphate Saturated with Sulphurous Acid on Haloid Salts.*—It is well-known that *cuprous iodide* is immediately precipitated when a solution of copper sulphate saturated with sulphurous acid is added to a solution of an iodide (Duflos, *Annalen*, 39, 253). Thus :—



Cuprous iodide was prepared by this method :—Two gram-molecules of copper sulphate were dissolved in 3 litres of water, the solution

saturated with sulphur dioxide, and 2 gram-molecules of potassium iodide dissolved in 150 c.c. of water were added. The pale yellow precipitate which was immediately formed was allowed to settle, the supernatant liquid poured off, and the residue washed with sulphurous acid solution by decantation until the whole of the sulphate had been removed; it was then boiled with water to render it granular, collected on linen, the product spread upon a porous tile, and finally exposed over sulphuric acid in a vacuum. Cuprous iodide retains moisture somewhat obstinately; after exposure for three weeks over sulphuric acid, a sample still contained 0.18 per cent. of moisture, but this was removed after further exposure. The dried iodide was reserved for future experiments.

One of the recognised methods of preparing *cuprous chloride* is very similar to the above. A solution of copper sulphate and potassium chloride is saturated with sulphur dioxide, when a crystalline, white precipitate of cuprous chloride is gradually deposited; excess of sulphurous acid, however, retards the precipitation of the chloride. If the clear solution is decanted from the precipitate and boiled, a further quantity is deposited. The cuprous chloride can be purified by washing it first with a solution of sulphurous acid and afterwards with glacial acetic acid, the product being then pressed between paper and dried in a warm place (Wöhler, *Annalen*, 1864, 130, 373; Rosenfeld, *Ber.*, 1879, 954).

Cuprous chloride cannot be washed by much water without undergoing decomposition, for as soon as the excess of acid is removed, the following interesting action begins in the presence of air, and, as was shown by Vogel, is rendered evident by the orange or red colour which the precipitate suddenly assumes:  $2\text{Cu}_2\text{Cl}_2 + \text{O} = \text{Cu}_2\text{O} + 2\text{CuCl}_2$ . Cuprous chloride can thus be almost completely decomposed by repeated treatment with water in the presence of air.

Freshly precipitated cuprous chloride is redissolved by sulphurous acid.

In view of the knowledge that both cuprous chloride and cuprous iodide can be prepared by the action of sulphur dioxide on a mixture of copper sulphate with potassium chloride or iodide in presence of water, it might be expected that *cuprous bromide* could also be prepared by a similar method. This we have found to be the case, although we have not met with any mention of this method of preparation (compare Dammer's *Handbuch der Anorg. Chemie*, 1894 edition). About 20 grams of copper sulphate and 8 grams of sodium bromide were dissolved in 300 c.c. of water, and sulphur dioxide passed in; after a time, small, white crystals were deposited. These were filtered rapidly from the mother liquor, washed with sulphurous acid, spread upon a porous tile, and then exposed over potassium hydroxide in a vacuum.

If the mother liquor was heated so as to expel sulphur dioxide, more crystals were deposited.

The crystals, which were pale greenish-yellow, subsequently became pale bluish-grey. The copper in the cuprous bromide was determined volumetrically.

0.662 corresponded with 0.5830 iodine.  $\text{Cu} = 44.29$ .

0.6740 gave 0.8808  $\text{AgBr}$ .  $\text{Br} = 56.00$ .

$\text{Cu}_2\text{Br}_2$  requires  $\text{Cu} = 44.21$  ;  $\text{Br} = 55.79$  per cent.

Cuprous bromide, like the chloride, is decomposed by water in the presence of air, but the action does not take place so readily. It also can be dissolved by sulphurous acid.

Both cuprous chloride and bromide may, therefore, be precipitated by the action of sulphur dioxide on solutions containing copper sulphate and a chloride or bromide ; and if the solution is but moderately concentrated (twice decinormal in the case of the bromide) the precipitation cannot be prevented, contrary to the statement of Fresenius, by the presence of excess of sulphurous acid.

It seemed, therefore, desirable to determine the *dilution necessary to prevent the precipitation of the chloride or bromide*. To ascertain this, 100 grams of copper sulphate were dissolved in 1 litre of water, and the solution saturated with sulphur dioxide. Twice normal solutions of potassium chloride, bromide, and iodide were made, and 10 c.c. of each added severally to 25 c.c. of the solution of cuprous sulphate in small stoppered flasks, and it was observed in each case whether a precipitate occurred or not. The haloid solutions were then diluted ten-fold, and again 10 c.c. of these were added severally to 25 c.c. of the same solutions of cuprous sulphate. Similar experiments were made when the haloid solutions were diluted one hundred-fold, a thousand-fold, &c. The results are recorded in Table I, p. 152.

On adding silver nitrate to the last solution, containing 0.000033 gram of potassium iodide, an opalescence was produced immediately.

From these experiments, it is clear that, whilst cuprous iodide, bromide, and chloride may all be precipitated by the addition of a haloid salt to a solution of cuprous sulphate, there is a great difference in their degree of solubility, cuprous iodide being much less soluble than the bromide, and, similarly, the bromide than the chloride. This explains the anomalous results sometimes obtained by students in the practice of qualitative analysis.

It is a common practice to remove iodine from a mixture of haloid salts by the addition of a solution of copper sulphate mixed with ferrous sulphate, as well as by the method already examined. Experiments similar to those described above were, therefore, made to test the



TABLE I.

KCl.	KBr.	KI.
1.5 grams. Little or no ppt. after 1 hour Crystals after 10 days.	2.4 grams. Ppt. within 1 minute.	3.3 grams. Immediate ppt.
0.15 gram. No ppt. after 10 days.	0.24 gram. Ppt. within 3 minutes.	0.33 gram. Immediate ppt.
	0.024 gram. Slight ppt. within 10 days	0.033 gram. Immediate ppt.
	0.0024 gram. No opalescence after 10 days	0.0033 gram. Immediate opalescence and gradual formation of a ppt.
		0.00033 gram. Immediate opalescence.
		0.000033 gram. No opalescence after 10 days

efficacy of this method; 100 grams of crystallised copper sulphate and 114 grams of ferrous sulphate were dissolved in 1 litre of water, and to 25 c.c. of this solution, placed in small stoppered flasks, were added as before, in each case, 10 c.c. of solutions of the haloid salt. The results are summarised in the following table.

TABLE II.

KCl.	KBr.	KI.
1.5 gram. No ppt.	2.4 grams. No ppt.	3.3 grams. Immediate ppt.
		0.33 gram. Immediate ppt.
		0.033 gram. Immediate ppt.
		0.0033 gram. Immediate opalescence and gradual formation of a ppt.
		0.00033 gram. No opalescence.

In each case, after standing some time, a little ferric hydroxide was precipitated.

A comparison of Tables I and II shows that a mixture of copper sulphate and ferrous sulphate is not nearly so liable to precipitate cuprous bromide and chloride along with iodide as a solution of copper sulphate saturated with sulphurous acid (the cuprous iodide may contain a little iron hydroxide.) Table II shows, moreover, that by securing a proper dilution it is very probable that cuprous iodide can be precipitated by a mixture of copper sulphate and ferrous sulphate, unaccompanied by cuprous bromide or chloride; if, further, the cuprous iodide, precipitated under such conditions, is collected and washed repeatedly with a solution of sulphurous acid, it is probable that every trace of cuprous bromide and chloride can be removed.

*A New Method of Preparing Cuprous Iodide.*—If copper foil is torn into shreds and heated in the presence of air in a porcelain basin over a Bunsen flame, and iodoform sprinkled over it in small quantities at a time, a violent action takes place, violet clouds of iodine being evolved, while a flame plays over the contents of the basin. The copper is then found to be coated with a black scale which is very readily peeled off, leaving a clean copper surface, and the copper may then be re-treated with iodoform until little or no metallic copper remains.

The black scale, on analysis, was found to contain a little carbon and cupric oxide, but it was almost wholly cuprous iodide (about 98 per cent.). On account of the difference in the properties of chloroform, bromoform, and iodoform, it is probable that by this method also cuprous iodide can be prepared entirely free from bromide or chloride.

#### *Preparation of Iodine from Cuprous Iodide.*

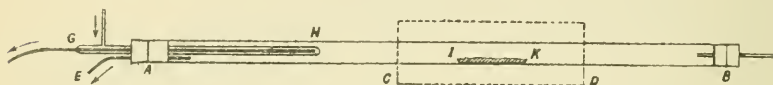
As already stated, one of us observed incidentally a few months ago that when cuprous iodide was heated in a current of carbonic anhydride no violet vapours appeared, although iodine was freely liberated if air or oxygen was substituted for the carbonic anhydride. It was found, also, that if carbonic anhydride free from air and dried by sulphuric acid was passed over cuprous iodide in a boat within a glass tube, and the iodide heated even until *fused*, no trace of iodine could be detected in the effluent gases by means of starch paper. Cuprous iodide can, therefore, in all probability be completely freed from moisture and from hydriodic acid by fusion in a current of carbonic anhydride.

Experiments showed, however, that if cuprous iodide was heated in a current of air, oxygen, nitric oxide, or nitrogen peroxide to temperatures between 200° and 300°, iodine was very readily liberated, the iodide at the same time becoming black. It appeared that the libera-

tion of the iodine was dependent on the oxidation of the copper:  $\text{Cu}_2\text{I}_2 + \text{O}_2 = 2\text{CuO} + \text{I}_2$ . We then endeavoured to ascertain (1) whether the whole of the iodine was liberated, (2) whether the action was dependent on the presence of moisture, and (3) whether the iodine liberated in this way from pure cuprous iodide was pure and free from iodic anhydride or any compound of copper.

The following apparatus was employed. A long piece of hard glass tubing, AB, heated by a gas furnace at C D, the temperature of which could be regulated by a thermostat, was connected at E with a water pump, so that air could be aspirated through the tube. GH was a

FIG. 1.



glass tube through which cold water circulated, providing a condensing surface for the iodine vapour, and IK was a porcelain boat containing cuprous iodide.

*Action of Gases at the Ordinary Temperature.*—The action of gases which liberate iodine from cuprous iodide with great readiness at elevated temperatures was tried at the ordinary temperature of the laboratory, the gases being dried by sulphuric acid. In no case, however, was sufficient iodine liberated to be condensed; its liberation in any particular case was only detected by starch paper introduced into the tube between A and C.

Air passed over cuprous iodide exposed to the light caused a slight coloration of the starch paper after 3 hours, and after 2 days the paper was quite blue. When air was passed over the iodide in the dark for 1 day, no iodine could be detected.

Oxygen did not liberate any iodine in the dark.

Nitric oxide and nitrogen peroxide each liberated iodine at once, both in the light and in the dark.

*Action of Air on Hot Cuprous Iodide.*—It was desirable to find the lowest temperature at which iodine could be liberated in sufficient quantity to be condensed and collected, so that the chance of volatilisation of cuprous iodide might be minimised (cuprous iodide boils at  $759-772^\circ$ ); below  $200^\circ$ , iodine was liberated only very slowly, but between  $220^\circ$  and  $240^\circ$ , a continuous stream of violet vapour was carried forward and condensed in beautiful crystals upon the condenser. Three experiments were made to test whether the whole of the iodine was expelled. In I, 2.5249 grams of cuprous iodide were heated at  $230-240^\circ$  for 11 hours; in II, 1.7101 grams were heated

to  $400^{\circ}$  for 18 hours, and in III, the cuprous iodide was heated at  $380^{\circ}$ . In I, 0.42, and in II, 0.15 per cent. of the iodide remained undecomposed. In No. III, the effluent vapours were passed into standard solutions of sodium thiosulphate, which were afterwards titrated with standard iodine solution; it was found that 22 per cent. of the iodine in the cuprous iodide was liberated in the first half-hour, 54 per cent. in the second half-hour, and 19 per cent. in the third half-hour, or 95 per cent. in  $1\frac{1}{2}$  hours; whilst after 6 hours more a small amount of iodine was still left in combination.

It is clear, therefore, that it is not easy to liberate the *whole* of the iodine from a given quantity of cuprous iodide, otherwise the relation  $\text{Cu}_2\text{I}_2 : 2\text{CuO}$  would connect in a way capable of exact determination the atomic weights of copper, iodine, and oxygen. Further experiments are being made on this point.

*Influence of Moisture on the Liberation of Iodine.*—When cuprous iodide was heated at  $240^{\circ}$  in air dried by passing it slowly through strong sulphuric acid, iodine was readily evolved. Experiments were then made to find whether air which had been more carefully dried

FIG. 2.



had the same effect. Tubes of the shape shown in the figure, made from soft glass tubing, were dried by heating them to  $200^{\circ}$ , and passing air dried by calcium chloride through them. A plug of glass wool, which had been dried at  $200^{\circ}$  for some hours, was placed at B, and the end A sealed. By means of a thistle funnel, about 1 gram of finely divided cuprous iodide, which had previously been fused and then allowed to cool in a current of carbonic anhydride, was introduced into C, and a plug of glass wool placed in D. A layer of phosphoric anhydride was next placed in E, and another plug of glass wool at F; the open end, G, was then drawn out, but not sealed. Two similar tubes were made; these were exhausted by a mercury pump and then sealed. Both tubes were heated for 10 days in a steam oven, and allowed to remain for four weeks more at the ordinary temperature.

In one of the tubes, the bulb C, containing the cuprous iodide, was heated at  $400^{\circ}$  for one hour, but no trace of iodine vapour could be seen.

Air which had been dried over phosphoric anhydride was introduced into the other tube, which was then again sealed. After two weeks, this second tube was heated to  $230^{\circ}$ , when violet vapours were

at once freely evolved and condensed on the cool portions of the tube. The experiments were repeated with similar results. It seemed, therefore, that the presence of water vapour was not essential to the action of air on cuprous iodide.

In order to ascertain whether water vapour alone had any action on cuprous iodide, steam was passed over hot cuprous iodide, but no iodine was liberated even when the iodide was fused.

*Purity of the Iodine Prepared from Cuprous Iodide.*—Iodine liberated as described from cuprous iodide at a temperature of  $240^{\circ}$  might conceivably contain a small quantity of some substance which would not be volatile at a much lower temperature, iodic anhydride, for example. Some of the iodine, 2.7529 grams, was therefore introduced into a short glass tube open at both ends, which was placed within a long wide tube heated to  $75^{\circ}$ , and a slow current of air passed through; after heating during four hours, a slight brown residue was left on the tube, weighing 0.3 milligram. It was found, however, that this residue was due to impurities in the air, as when the air passed over the cuprous iodide and that in which the iodine volatilised, was filtered through cotton wool, the surface of the tube remained perfectly clean, and no change of weight could be detected.

In order to show that the iodine did not contain any compound of copper, the violet vapours liberated from cuprous iodide at  $240^{\circ}$  were mixed with coal gas and air and the mixed gases burnt at the mouth of a glass tube. On examining the flame spectroscopically, no evidence of the characteristic copper bands could be detected, whilst they at once became visible when a copper wire was held in the flame.

The melting point (uncorrected) of the iodine, determined in the usual way, was found to be  $112.5$ — $114^{\circ}$ . It has a blacker appearance than commercial iodine, and does not so readily emit violet vapours.

### *Conclusions.*

From the results of these experiments, it is evident—

1. That cuprous iodide can be prepared free from cuprous bromide or chloride.
2. That cuprous iodide can be heated without decomposition and completely dried in an atmosphere of carbonic anhydride.
3. That when dry air is passed over cuprous iodide heated at  $240^{\circ}$  the iodine is liberated and can readily be condensed.
4. That the iodine obtained in this way is free from any compound of copper.

Whether such iodine is as pure or not as that prepared by Stas by other methods, in which one main difficulty was the drying of the



iodine and the removal of hydriodic acid, it appears desirable to re-determine the atomic weight of the element prepared by this entirely distinct method.

It may be added that iodine is also readily liberated, in a similar way, from palladious iodide, but owing to the costliness of this substance a detailed examination of the action has not been made.

OWENS COLLEGE AND ACKWORTH SCHOOL,  
January, 1898.

### IX.—*Action of Alkalies on Amides.*

By JULIUS B. COHEN, Ph.D., and CHARLES EDWARD BRITTAIN, B.Sc.,  
The Yorkshire College.

COHEN and ARCHDEACON (Trans., 1896, 69, 91) have shown that many amides of aromatic bases form additive compounds with sodium alcoholates containing 1 mol. of amide in combination with 1 mol. of the alcoholate.

That analogous compounds might exist containing sodium or potassium hydroxide in place of the alcoholate was a natural inference, but every attempt to prepare them by the usual method employed in the case of the alcoholates was unsuccessful. In the latter case, the addition of the alcoholate to the amide suspended in ether, as a rule, yielded a clear solution, which, after a short time, deposited the crystalline additive compound. If powdered caustic soda is added to acetanilide dissolved in ether, the alkali remains undissolved, and on filtering and evaporating the solution, the unchanged amide is deposited. An attempt to precipitate the additive compound by adding a concentrated alcoholic solution of the alkali to the ethereal solution of the amide proved equally unsuccessful, the mixture remaining perfectly clear, and on evaporation at the ordinary temperature depositing a flocculent precipitate, which did not invite further investigation. We then adopted another method which had been found useful in the preparation of alcoholates where the amide was only slightly soluble in ether. In this case, the powdered sodium alcoholate was added to the powdered amide suspended in ether, and, after shaking well, the liquid was filtered; on standing, the additive compound crystallised from the clear solution. During the process of shaking caustic soda with acetanilide in ether, a very noticeable change was observed. Both powdered caustic soda and acetanilide alone, after being shaken up in ether, rapidly subside; but when the two are mixed together, a bulky, light, and apparently homogeneous powder is produced quite distinct in character from either constituent. On filtering, a small quantity of a crys-

talline deposit appeared in the ether, which, when decomposed with water, gave a strongly alkaline reaction, but the analytical results obtained with different preparations did not agree, and the quantity of alkali was invariably too low. Exactly the same thing occurred in the case of paracetotoluidide.

In spite of these indefinite results, the existence of additive compounds seemed sufficiently clearly indicated to justify further experiments. It appeared probable that an amide more soluble in ether than either acetanilide or paracetotoluidide might be more suitable for the purpose, and this view has proved to be correct.

We first selected paracetobromotoluidide, as it is comparatively soluble in ether, and, although the yield was small, we obtained very satisfactory results by a method similar to that just described. After repeated trials, with the object of improving the yield by the use of different solvents, we returned to the original method, which, with slight modifications, has been adopted throughout.

An excess (about 1 gram) of clean caustic soda is placed in a mortar under a layer of dry ether and finely powdered; 1 gram of the amide in powder is then added and well mixed with the alkali for a few moments. The sodium hydroxide compound, like the alcoholate compound, first dissolves and then rapidly crystallises out. By selecting the moment at which solution occurs, and filtering before the new compound has time to separate, a clear solution is obtained which immediately begins to deposit crystals. The mixture is filtered into a weighed flask, the ether is decanted as soon as the crystals have separated, and the latter, after being washed once or twice with ether by decantation, are dried in a vacuum and weighed. The substance is then decomposed by water and the amount of alkali determined by titration with decinormal hydrochloric or oxalic acid solution.

In all cases, well-defined crystals were obtained, and occasionally transparent needles a quarter of an inch long.

These compounds exhibit considerable differences in solubility in ether. Thus the sodium hydroxide compound of acetanilide, paracetotoluidide, and  $\alpha$ -acetophthalide are nearly insoluble, whereas those obtained from ortho- and para-acetobromotoluidide and potassium hydroxide only deposit the additive compound on concentrating the ethereal solution; apparently the potassium hydroxide compounds are much more soluble than the corresponding sodium hydroxide compounds.

They are all decomposed by water, or more or less rapidly in contact with moist air, and, like the corresponding alcoholates, may be dissociated, not only in boiling ether, but even in some cases by washing with cold ether; this occurs notably in the case of the bromine derivatives of the amides, probably by reason of their greater solubility, whereas the amides themselves are not affected in this way.

The following amides appear to form additive compounds with caustic soda, but only those have been analysed which gave a satisfactory yield of the pure product.

Acetanilide, acetobromanilide, acetiodanilide, paracetotoluidide, paracetobromotoluidide, orthoacetotoluidide, orthoacetobromotoluidide,  $\alpha$ -acetophthalide,  $\alpha$ -acetobromophthalide,  $\beta$ -acetophthalide,  $\beta$ -acetobromophthalide.

The potassium hydroxide compounds of ortho- and para-acetobromotoluidides have also been investigated.

It would have been a simple matter to have multiplied examples ; but the results obtained convinced us that the reaction was of a general character, and that the compounds were of a perfectly definite type.

Apart from a certain theoretical interest which attaches to these compounds and which is discussed further on, they form a class which, we believe, has no analogues among inorganic or organic substances, for they may be regarded as containing the sodium and potassium hydroxide in the loose form of combination which is exhibited by water, alcohol, or benzene of crystallisation.

Another point of interest is the fact that, as the alkali readily dissolves in ether in presence of certain of the amides, and as the former retains its alkaline character unchanged in this solution, an ethereal solution of caustic alkali is thereby obtained, which may be found applicable as a reagent where aqueous or alcoholic potash or soda do not fulfil the requirements of the reaction. We have, for example, attempted to prepare glycol from ethylenic bromide in this manner. On boiling up an ethereal solution of paracetobromotoluidide potassium hydroxide with rather more than the calculated quantity of ethylenic bromide for several hours, potassium bromide separated, and the liquid became neutral ; the potassium bromide, after being collected and carefully washed with ether, was extracted with a small quantity of propylic alcohol in the cold, and the alcohol filtered and evaporated, when a small quantity of a viscid liquid was left. As the ethereal solution might also contain a little glycol, it was shaken up with water ; on evaporating the water, a few crystals of acetobromotoluidide separated (m. p.  $118^{\circ}$ ), together with some globules of liquid. The latter were separated by again extracting with water and evaporating, but the liquid thus obtained was so small in quantity that it could not be further examined, although it is not improbable that the substance is glycol. By the action of chloroform on boiling ethereal solution of orthoacetobromotoluidide sodium hydroxide, the liquid became neutral, and sodium chloride mixed with a crystalline compound separated. There was a faint smell of isocyanide, but no formic acid was formed. The compound which separated, along with the common salt, was at first

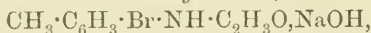
thought to be acetobromotoluidide as it had the same melting point, but it is much less soluble in ether, and insoluble in boiling water; moreover, it crystallises in feathery tufts and not in needles. We briefly mention these facts, as some little time may elapse before it will be possible to continue this investigation.

*Paracetobromanilide sodium hydroxide*,  $C_6H_4Br \cdot NH \cdot C_2H_3O, NaOH$ .—One gram of finely powdered acetobromanilide was added to an excess of caustic soda finely ground under ether, and the whole well mixed. The ether was then filtered into a weighed flask, corked, and allowed to stand 12 hours; after decanting the ether from the crystalline deposit, the latter was dried in a vacuum, weighed, and analysed.

0.183 gram required 6.8 c.c. of N/10 oxalic acid. Na = 8.55 per cent.

$C_6H_4Br \cdot NH \cdot C_2H_3O, NaOH$  requires Na = 9.0 per cent.

*Paracetobromotoluidide sodium hydroxide*,



was prepared as above described, but crystallised from the ethereal solution more readily than the corresponding anilide. The following results were obtained.

I.	0.192	gram	required	7.5	c.c.	N/10	hydrochloric	acid.	Na = 8.9.
II.	0.214	"	"	8.1	"	"	"	"	Na = 8.7.
III.	0.115	"	"	4.6	"	"	"	"	Na = 9.0.
IV.	0.124	"	"	4.7	"	"	"	"	Na = 8.7.

The average on the four determinations is Na = 8.8 per cent.

$CH_3 \cdot C_6H_3Br \cdot NH \cdot C_2H_3O, NaOH$  requires Na = 8.6 per cent.

*Paracetobromotoluidide potassium hydroxide*,



is very soluble in ether, for the whole of the amide in combination with the potassium hydroxide dissolves. One gram of the acetobromotoluidide was ground up with an excess of potash under ether, filtered, and the ether evaporated in a vacuum; the residue weighed 1.223 grams (calculated 1.24 grams). It is a comparatively stable compound, and requires to be boiled with water some time before it is completely decomposed; the residue on titration required 38 c.c. N/10 oxalic acid; K = 12.1 per cent. (calculated 13.7). A purer product was prepared by partially evaporating the ether, allowing a portion of the compound to crystallise, and draining this on a porous plate. The following results were then obtained.

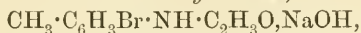
I.	0.401	gram	required	14	c.c.	N/10	oxalic	acid.	K = 13.6	per cent.
II.	0.3355	"	"	11.6	"	"	"	"	K = 13.5	"

$CH_3 \cdot C_6H_3Br \cdot NH \cdot C_2H_3O, KOH$  requires K = 13.7 per cent.

*Orthoacetotoluidide sodium hydroxide*,  $\text{CH}_3 \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{C}_2\text{H}_5\text{O}, \text{NaOH}$ , which was prepared in the usual way, on titration with N/10 oxalic acid, gave  $\text{Na} = 12.2$  per cent. in each of two experiments.

$\text{CH}_3 \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{C}_2\text{H}_5\text{O}, \text{NaOH}$  requires  $\text{Na} = 12.17$  per cent.

*Orthoacetobromotoluidide sodium hydroxide*,



is very soluble in ether, and considerable difficulty was experienced in obtaining a pure preparation. When the ethereal solution was evaporated, some of the free toluidide crystallised at the same time, and the percentage of sodium was generally about 1 per cent. too low. Attempts to precipitate the compound by adding to the ethereal solution indifferent solvents such as chloroform or benzene proved fruitless. The following method was finally adopted; the sodium hydroxide was powdered under about 10 c.c. of ether, transferred to a flask, and the acetobromotoluidide added in quantities of about 0.25 gram, being well shaken after each addition. The toluidide dissolved readily at first, more slowly after 0.75 gram had been added, and very soon crystallisation of the sodium hydroxide compound was observed. At this point, the liquid was rapidly filtered, and left to crystallise.

0.089 gram required 3.45 c.c. N/10 oxalic acid.  $\text{Na} = 8.9$  per cent.

$\text{CH}_3 \cdot \text{C}_6\text{H}_3\text{Br} \cdot \text{NH} \cdot \text{C}_2\text{H}_5\text{O}, \text{NaOH}$  requires  $\text{Na} = 8.6$  per cent.

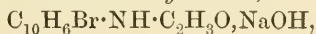
*Orthoacetobromotoluidide potassium hydroxide*,



like the para-compound, is exceedingly soluble in ether, but differs from the latter in forming a non-crystalline glassy mass on evaporating the ethereal solution; it was therefore impossible to purify the product. Like the para-compound also, it is only slowly decomposed by water, and requires to be boiled with it for some time before complete decomposition is effected. A rough determination of the composition of the substance was effected by shaking up 0.25 gram of the amide with an excess of potash in ether, filtering, evaporating the ether, and titrating the product. It required 9.85 c.c. N/10 oxalic acid.  $\text{K} = 12.4$  per cent. (calculated 13.7 per cent.). The low result is no doubt due to presence of uncombined amide.

*α-Acetonaphthalide sodium hydroxide*,  $\text{C}_{10}\text{H}_7 \cdot \text{NH} \cdot \text{C}_2\text{H}_5\text{O}, \text{NaOH}$ , crystallises very rapidly, and the ethereal solution must be filtered as quickly as possible after mixing the amide with the alkali. A mean of four titrations with N/10 hydrochloric acid gave  $\text{Na} = 10.23$ .  $\text{C}_{10}\text{H}_7 \cdot \text{NH} \cdot \text{C}_2\text{H}_5\text{O}, \text{NaOH}$  requires  $\text{Na} = 10.2$  per cent.

*α-Acetobromonaphthalide sodium hydroxide*,

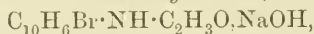




is fairly soluble in ether and crystallises slowly on standing. A mean of three titrations with N/10 oxalic acid gave  $\text{Na} = 7.5$  per cent.  $\text{C}_{10}\text{H}_6\text{Br}\cdot\text{NH}\cdot\text{C}_2\text{H}_3\text{O}, \text{NaOH}$  requires  $\text{Na} = 7.5$  per cent.

*$\beta$ -Acetonaphthalide sodium hydroxide*,  $\text{C}_{10}\text{H}_7\cdot\text{NH}\cdot\text{C}_2\text{H}_3\text{O}, \text{NaOH}$ .—The mean of four titrations with N/10 oxalic acid gave  $\text{Na} = 10.2$  per cent.  $\text{C}_{10}\text{H}_7\cdot\text{NH}\cdot\text{C}_2\text{H}_3\text{O}, \text{NaOH}$  requires  $\text{Na} = 10.2$  per cent.

*$\beta$ -Acetobromonaphthalide sodium hydroxide*,



dissolves easily in ether, but does not crystallise readily, and a pure product could not be obtained.

On account of the ready solubility of the potash compound of paracetobromotoluidide in ether, it was chosen in order to study the action of various reagents on it. When iodine dissolved in ether is allowed to drop into an ethereal solution of the potash compound it is immediately decolorised, and a crystalline mixture of potassium iodide and iodate separates. The action of iodine on the substance is therefore the same as on aqueous potash. A small quantity of iodoform was also detected; and this, which was also observed in the case of acetanilide sodium methoxide, is probably due in both cases to the decomposition of the ether in presence of the alkali.

By the action of acetic chloride in slight excess in the cold, both potassium chloride and potassium acetate were formed, so that both free acetic acid and free hydrochloric acid must be produced at the same time. Benzoic chloride acts similarly; the theoretical quantity of benzoic chloride yielded a mixture of potassium chloride and benzoate, together with free hydrochloric and benzoic acids. Thus:

1.  $\text{CH}_3\cdot\text{C}_6\text{H}_3\text{Br}\cdot\text{NH}\cdot\text{C}_2\text{H}_3\text{O}, \text{KOH} + \text{C}_6\text{H}_5\cdot\text{COCl}$   
 $= \text{CH}_3\cdot\text{C}_6\text{H}_3\text{Br}\cdot\text{NH}\cdot\text{C}_2\text{H}_3\text{O} + \text{C}_6\text{H}_5\cdot\text{COOH} + \text{KCl}.$
2.  $\text{CH}_3\cdot\text{C}_6\text{H}_3\text{Br}\cdot\text{NH}\cdot\text{C}_2\text{H}_3\text{O}, \text{KOH} + \text{C}_6\text{H}_5\cdot\text{COCl}$   
 $= \text{CH}_3\cdot\text{C}_6\text{H}_3\text{Br}\cdot\text{NH}\cdot\text{C}_2\text{H}_3\text{O} + \text{HCl} + \text{C}_6\text{H}_5\cdot\text{COOK}.$

The theoretical bearings of these compounds on the constitution of the amides has been discussed in the paper by Cohen and Archdeacon (*loc. cit.*); what has been stated there applies with equal force in the present case. If we are to regard these substances as anything more than 'molecular' compounds, the following formula must be assigned to them,  $\text{CH}_3\cdot\overset{\text{R}'\cdot\text{N}\cdot\text{Na}}{\underset{\text{C}(\text{OH})_2}{\text{C}}}$ , for there can be no doubt as to the strict analogy which exists between them and compounds of the amides with sodium alcoholate.

This constitution of the sodium alcoholate compound has recently been disputed by Hantzsch (*Annalen*, 1897, 296, p. 61) who prefers the

following formula, 
$$\text{CH}_3 \cdot \overset{\text{R} \cdot \text{NH}}{\underset{\cdot}{\text{C}}} \begin{cases} \text{ONa} \\ \text{OC}_2\text{H}_5 \end{cases}$$
, but this view can scarcely be

reconciled with the fact that, by heating the substance on the water bath, it loses a molecule of alcohol and yields sodium acetanilide (Seifert, *Ber.*, 1885, 18, 1358), and that the latter, by the action of methylic iodide, can be readily converted into methylacetanilide and finally into methylaniline.

Hantzsch's formula would necessitate a molecular change of a very complex character, which is scarcely justified by the facts.

### X.—*Formation of Monomethylaniline from Dimethylaniline.*

By JULIUS B. COHEN, Ph.D., and HARRY T. CALVERT, B.Sc., The  
Yorkshire College.

THE conversion of a tertiary aromatic base into a derivative of a secondary base has been observed by Hess (*Ber.*, 1885, 18, p. 685), who found that, by boiling dimethylaniline with benzoic chloride, benzoylmethylaniline is formed, and the methyl group eliminated as methylic chloride. A similar reaction was described by Staedel (*Ber.*, 1886, 19, 1947), who showed that acetic bromide converts dimethylaniline into acetylmethylaniline. In neither case are the yields given. We find that the conversion of dimethyl- into monomethyl-aniline may be effected in quite another way.

In attempting to elucidate the constitution of the substance which we described a short time ago under the name of *phenylnitrocarbinol* (*Trans.*, 1897, 71, 1050), we studied its behaviour with various substances, and found that, in most cases, its action closely resembled that of nitrous acid, which is scarcely remarkable, seeing that phenylnitrocarbinol evolves nitrous fumes on standing. Its action on dimethylaniline is, however, sufficiently curious to merit a brief description.

On adding phenylnitrocarbinol to an equivalent quantity of dimethylaniline, the mixture becomes very dark coloured, and the temperature rises rapidly, whilst at the same time there is a rapid evolution of nitrogen gas entirely free from carbon dioxide.

This evolution of gas occurs whether the mixture is cooled down or allowed to become hot, and the quantity appears to be independent of temperature and, within certain limits, of the amount of dimethylaniline present.

In one experiment, 1.0015 grams of phenylnitrocarbinol and 2 grams of dimethylaniline gave 13.5 c.c. of gas, and, in a second experiment, performed under similar conditions, 2.2225 grams of the nitrocarbinol gave 27 c.c. of gas, the proportion of substance and gas being in both cases the same. The product of the action, which is deep red by transmitted light and a deep green by reflected light, was mixed with sufficient hydrochloric acid to combine with the unchanged dimethylaniline, and then extracted with ether. By adding sodium carbonate to the acid solution and distilling with steam, the unchanged dimethylaniline could be recovered; the tarry liquid which remained in the distilling vessel did not invite further investigation.

The ethereal extract contains benzaldehyde, benzylic alcohol, and nitrosomethylaniline. Four experiments, in each of which 30 grams of phenylnitrocarbinol were employed, gave on the average 5 grams of benzaldehyde, 4.5 grams of benzylic alcohol, and 5.5 grams of nitrosomethylaniline. Thus about half of the nitrocarbinol disappears, and is probably represented by the tarry material already referred to.

That the nitrosomethylaniline is not due, as was at first supposed, to the presence of methylaniline in the dimethylaniline used, was shown by the fact that a sample of dimethylaniline which had been carefully freed from monomethylaniline gave a result precisely similar to the above.

The three substances contained in the ether were separated and identified, as follows. The ethereal extract was treated with sodium hydrogen sulphite solution until nothing further crystallised. The ethereal solution was then separated from the bisulphite compound, the ether removed by distillation, and the residue distilled with steam; an oil of a yellow colour, and possessing the fragrant smell of nitrosomethylaniline, passed over, leaving a yellow, crystalline compound in the distilling flask, and this, when recrystallised from water, formed brilliant, golden plates which melted with decomposition at  $150^{\circ}$ . The minute quantity of this crystalline compound precluded its further investigation.

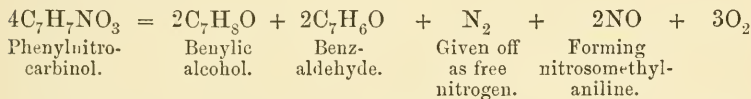
The nitrosomethylaniline was extracted from the distillate by ether, the ether removed, and the residual oil warmed with  $2\frac{1}{2}$  times its weight of stannous chloride previously dissolved in three times the quantity of strong hydrochloric acid; the nitrosomethylaniline is thus reduced to methylaniline and remains in solution, whereas the whole of the benzylic alcohol is converted into benzylic chloride and separates as an oil. The liquid is then diluted with water and distilled in a current of steam. The benzylic chloride which distils was identified by converting it into benzaldehyde, and the latter into the phenylhydrazone melting at  $153^{\circ}$ . The solution of methylaniline was made alkaline with caustic soda, extracted with ether, and the ethereal solution,

after dehydrating over potash, was distilled; the methylaniline thus obtained was then converted into the platinochloride, which gave the following result on analysis.

0.1358 gave 0.0438 Pt. Pt = 31.2 per cent.

$(C_7H_9N)_2, H_2PtCl_6$  requires Pt = 31.4 per cent.

It is difficult to formulate in any satisfactory fashion the above reaction. If we assume that the half, of the nitrocarbinol which is converted into tar, has been oxidised at the expense of the other half, then the equation



will represent very closely the quantities involved. What becomes of the methyl group which is detached from the dimethylaniline cannot be at present explained, seeing that no carbon dioxide is formed.

The evolution of nitrogen is generally associated either with the action of a nitroso- on an amido-group or with the decomposition of a diazo-compound, which practically represents an intermediate stage of the same process. As there appears no reason to anticipate the formation of a diazo-compound, we are led to assume that the first process is responsible for the production of nitrogen. This could only occur by the reduction of an original nitro- or nitroso-group to an amido-group, that is, by the reduction of the nitrocarbinol to benzylamine, which, by the action of nitrous acid evolved from another molecule of the nitrocarbinol would produce benzylic alcohol, whilst benzaldehyde would be formed simultaneously. By what chemical change the reduction occurs, it is impossible at present to conjecture.

#### *Action of Nitrogen Trioxide on Dimethylaniline.*

The above result suggested the possibility of a similar reaction occurring when nitrogen trioxide acts on dimethylaniline in an indifferent solvent. A brief reference to the action of nitrogen trioxide on dimethylaniline dissolved in alcohol or acetic acid occurs in a paper by Lippmann and Lange (*Ber.*, 1880, 13, 2136), in which they state that the base is partly converted into a resinous matter (*partielle Verharzung*). Having a small quantity of the trioxide dissolved in chloroform at hand, the gas was driven over into a solution of dimethylaniline dissolved in ether by a current of nitric oxide in order to remove traces of the peroxide. The ether rapidly changed colour, passing from green to black, and a black and sticky deposit ultimately separated. This method was afterwards modified, and liquid nitrogen

trioxide\* was allowed to drop into the dimethylaniline dissolved in five times its weight of dry ether.

Each drop of the trioxide on coming in contact with the ether produced a hissing noise like a red-hot wire plunged into water, but in spite of the apparent vigour of the action, there was a scarcely perceptible rise of temperature. In both cases, the same result was obtained.

In order to test the product for nitrosodimethylaniline, the ether, which was coloured brown, was decanted from the black deposit, shaken with hydrochloric acid to remove dimethylaniline, the ether removed by distillation, and the residue distilled with steam. The aqueous distillate was yellow; but no drops of oil were visible, and no smell of nitrosomethylaniline could be detected. The distillate was extracted with ether, and the minute quantity of residue left on removing the ether gave no nitroso-reaction. Nitrosodimethylaniline is therefore not formed by this reaction, and the action of nitrogen trioxide is distinct from that of phenylnitrocarbinol.

In the distilling flask, a small quantity of yellow, needle-shaped crystals separated, which were apparently identical with the substance obtained in the action of phenylnitrocarbinol on dimethylaniline, and previously referred to.

The black, tarry-looking product, although of such an uninviting appearance, is nevertheless easily purified; it was first extracted with small quantities of benzene until the latter was nearly colourless. A little resinous matter is thereby removed; and as prolonged boiling with alcohol decomposed the substance, the residue was repeatedly extracted with small quantities of alcohol just heated to boiling. On cooling, long, steel blue needles separate; these decompose with slight explosion when heated, evolving nitrous fumes. The substance dissolves readily in alcohol and in water with a bright yellow colour. On boiling with glacial acetic acid for a short time, a rapid evolution of nitrous fumes takes place, and the product, which contains nitrogen, when poured into water forms a yellowish-green, crystalline mass, consisting of fine needles. These, when recrystallised from dilute alcohol, are pale brown, and melt at 155—157°.

As these products are readily obtainable, we have thought it worth while to investigate more fully this somewhat curious reaction, which we reserve for a future communication.

\* The liquid trioxide is most conveniently prepared by acting upon arsenic trioxide with ordinary concentrated nitric acid, whereby a considerable quantity of peroxide is formed, and allowing the gas to meet a current of pure and dry nitric oxide on its way to the cooled receiver. If a more dilute nitric acid is used, the yield is very much diminished, as the gas evolved consists mainly of nitric oxide. By operating in the manner described, the trioxide is obtained of a pure blue colour.



It is interesting to note the entire dissimilarity between the action of anhydrous nitrogen trioxide and that of its aqueous solution, and it seems not unlikely that analogous results may be met with in the case of other bases, and possibly also in the case of phenols.

## XI.—*Volumetric Estimation of Sodium.*

By HENRY J. HORSTMAN FENTON, M.A.

### *Titration of Dihydroxytartaric Acid with Potassium Permanganate.*

WHEN a few drops of potassium permanganate solution are run into a solution of dihydroxytartaric acid, mixed with excess of dilute sulphuric acid, at the ordinary temperature, there is at first no apparent change. After standing for a few minutes, however, the colour is discharged, and on continuing the addition of permanganate, the action, when once started, proceeds rapidly, the behaviour being in this respect analogous to that of hydrogen dioxide when similarly treated. The change becomes somewhat slower as it approaches completion, but the end point is well marked and definite.

The relation between dihydroxytartaric acid and permanganate will be seen from the following results. Using a solution of permanganate containing 3.200 grams  $\text{KMnO}_4$  per litre,

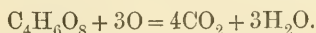
Gram acid taken.	c.c. $\text{KMnO}_4$ .	Gram $\text{KMnO}_4$ .	Atoms of oxygen required for 1 mol. acid.
0.3160	99.7	0.31904	2.90
0.2932	92.3	0.29536	2.90
0.1409	44.2	0.14144	2.89
0.2506	78.6	0.25152	2.89

and with a solution containing 6.3374  $\text{KMnO}_4$  per litre,

0.3145	49.9	0.31624	2.89.
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Taking the mean of these five observations, 1 gram  $\text{KMnO}_4 = 0.99405$  gram  $\text{C}_4\text{H}_6\text{O}_8$ , or 182 grams  $\text{C}_4\text{H}_6\text{O}_8 = 183.09$  grams  $\text{KMnO}_4$ .

If the acid were entirely oxidised to carbon dioxide and water, 3 atoms of oxygen would be required for 1 molecule of acid



The difference observed may be due, in part, to the fact that an aqueous solution of the acid undergoes a slight decomposition, even at ordinary temperatures, into tartronic acid and carbon dioxide. In the experiments recorded in a former communication (Part I., Trans., Jan., 1898), it was observed that small quantities of carbon dioxide could be traced after the solution had been standing for about 10 or 12 minutes,

and this is about the usual duration of the experiment when titrating the acid with permanganate. It is true that tartronic acid also reduces permanganate, but the initial stage, at the ordinary temperature, is extremely slow. Thus 0.1625 gram of tartronic acid took about 50 minutes to bleach 1 c.c. of a solution of permanganate containing 0.0032  $\text{KMnO}_4$  per c.c.\*

In any case, the relation between dihydroxytartaric acid and permanganate is a perfectly definite one, and it will be shown that the reaction affords a very convenient method for the estimation of the acid or its salts.

### *Volumetric Estimation of Sodium.*

Bearing in mind the very sparingly soluble character of sodium dihydroxytartrate, and the definite relation between potassium permanganate and dihydroxytartaric acid, it appeared probable that a simple method might be devised for the quantitative estimation of sodium by a volumetric process.

In the first experiments, measured volumes of a standard solution of pure sodium chloride were mixed with excess of dihydroxytartaric acid dissolved in a small quantity (about 10 c.c.) of water; the mixture was made just ammoniacal and allowed to stand, with frequent stirring, for times varying from 10 to 75 minutes. The precipitated sodium salt was then collected, and after being drained with the aid of the pump was washed three times with small quantities of water, draining well each time; the precipitate was then dissolved off the filter with a considerable excess of dilute sulphuric acid, and the mixture titrated with permanganate.

In recording the results, it will be convenient to denote the quantities by the following symbols.

$a = \text{NaCl taken (gram)}$ ;  $b = \text{KMnO}_4$ , solution required (c.c.);  $c = \text{Na found (gram)}$ ;  $d = \text{Na calculated (gram)}$ .

In the first trial experiment, the precipitation and washing were carried out at the *ordinary temperature*.

Strength of permanganate solution = 3.200  $\text{KMnO}_4$  per litre (sol. A).  
Strength of sodium chloride solution = 49.629  $\text{NaCl}$  per litre.

$a.$	$b.$	$c.$	$d.$
0.24814	114.2	0.0918	0.0975

\* The difference is probably due also to traces of non-oxidisable impurity (water or acetic acid, for example) in the samples of dihydroxytartaric acid employed, since subsequent experiments show that when the potassium salt is used instead of the free acid, the oxygen value approaches more nearly to 3 atoms. The potassium salt crystallises extremely well, so that results obtained by its use are probably more trustworthy. It will be seen, however, that the numerical value of the oxygen ratio in no way affects the final results in the estimation of sodium.

It has been previously shown (Part I.), in the experiments on titration by alkalis, that the salts of dihydroxytartaric acid undergo a considerable amount of decomposition in contact with water at the ordinary temperature, so that a low result was here to be expected.

In the following experiments, both the sodium salt and the dihydroxytartaric acid solutions were carefully *cooled by ice* before mixing, the mixture was allowed to stand in ice during precipitation, and the precipitate was washed with ice-cold water. The advantage of operating at  $0^{\circ}$  is not only that the decomposition of the salt is prevented (as previously shown), but that the solubility of the sodium salt at this temperature is exceedingly small. The solubility, as will be pointed out later on, is 0.039, at  $0^{\circ}$ , that is, 100 parts of water dissolve 0.039 part of the sodium salt, which is equivalent to 0.0064 part of sodium. The total volume of the filtrate and washings in each experiment usually amounts to about 25–40 c.c., so that, even in pure water, the amount of sodium dissolved would be almost negligible; but the solubility is of course still further diminished by the presence of excess of dihydroxytartrate, that is, in a solution containing a common ion.

	<i>a.</i>	<i>b.</i>	<i>c.</i>	<i>d.</i>
I.	0.24814	120.2	0.0966	0.0975
II.	0.24814	60.5	0.0963	0.0975

III took 65.5 c.c., and IV took 60.6 c.c. of permanganate.

In II, III, and IV, a fresh solution of permanganate was now employed, containing 6.3375  $\text{KMnO}_4$  per litre (solution B). The times of precipitation, in minutes, were 15, 25, 75, and 45 respectively.

Although these results were constant and not much below the theoretical values, the process was hardly considered satisfactory, since, on further trial, it was found that excess of ammonia considerably vitiated the results, and exact neutralisation is not easy. Experiments were then made using pure *potassium carbonate* (prepared from potassium bitartrate) in calculated quantity for neutralisation in place of ammonia. The mixture was also made more concentrated, the acid being now dissolved in about 2 c.c. of water, instead of in 10 c.c. A fresh solution of sodium chloride was prepared containing 40 grams  $\text{NaCl}$  per litre, the permanganate used being the same as in the previous experiments (solution B). Five c.c. of  $\text{NaCl}$  solution were used, as before, for each experiment.

	<i>a.</i>	<i>b.</i>	<i>c.</i>	<i>d.</i>
V.	0.200	52.1	0.0815	0.0786

VI took 53 c.c., and VII 54 c.c. The times of precipitation were 30, 60, and 150 minutes respectively. Using twice the previous

proportion of dihydroxytartaric acid and potassium carbonate, the results were still higher, VII taking 57.3 c.c.

Substituting *ammonium carbonate* for potassium carbonate, similarly high results were obtained, VIII requiring 52.8 c.c.

The explanation of these high results when potassium or ammonium carbonates are used in concentrated solutions is found in the fact, subsequently discovered, that potassium and ammonium dihydroxytartrates, although fairly easily soluble at ordinary temperatures, dissolve with difficulty at 0° and thus tend to contaminate the precipitated sodium salt. This source of error would be avoided, and the process much simplified, by employing one of these salts for precipitation instead of using the free acid and subsequently neutralising.

The preparation and composition of the potassium and ammonium salts were therefore studied, with the results which will be given in a subsequent communication.

The potassium salt is easy to prepare, and appears to be quite permanent if kept in a closed vessel (it is also fairly permanent in the air, for some days, at any rate). It is likewise somewhat less soluble than the ammonium salt, so that its use does not involve any danger of contamination with ammonium, should salts of the latter be present. The potassium salt is, in fact, a most convenient reagent both for the qualitative and quantitative estimation of sodium.

Using the same sodium chloride and permanganate (B) solutions as before, and precipitating with excess (about  $1\frac{1}{2}$  equivalents) of the potassium salt, the following results were obtained.

<i>a.</i>	<i>b.</i>	<i>c.</i>	<i>d.</i>
0.200	49.4	0.0786	0.0786
0.200	48.4	0.0770	0.0786
0.200	48.8	0.0776	0.0786

Since measurement of the strong sodium chloride solution was probably hardly sufficiently accurate, in the next experiments weighed quantities of sodium chloride, each dissolved in 5 c.c. of water, were employed instead of measured volumes of standard solution.

<i>a.</i>	<i>b.</i>	<i>c.</i>	<i>d.</i>
0.0997	23.5	0.0374	0.0391
0.1915	47.6	0.0757	0.0752
0.4367	107.4	0.1710	0.1716

The process, therefore, when conducted in this manner, evidently gives satisfactory results.

The permanganate solutions employed so far had been standardised by means of ammonium oxalate, and the results were calculated from the relations shown to exist between permanganate, dihydroxytartaric

acid and sodium. In preparing a fresh permanganate solution (solution C) for subsequent experiments, it appeared that the most direct way would be to standardise the solution by means of pure sodium chloride. The following were the observations.

$S$  = strength of permanganate (C) in grams of Na *per litre*.

<i>a.</i>	<i>b.</i>	<i>S.</i>
0.2235	49.4	1.778
0.1865	40.4	1.814
0.3704	79.9	1.822
0.3032	66.2	1.800

Mean of the four experiments,  $S = 1.805$ .

This solution was now employed for the estimation of sodium in various common sodium salts.

*Normal Sodium Sulphate.*—This was a commercially pure specimen recrystallised and ignited. 0.3472 gram of substance, dissolved in about 5 c.c. of water and precipitated with excess (1 gram) of potassium dihydroxytartrate, required 62.75 c.c. of permanganate (C). Na Found = 32.62 per cent., Calculated 32.39 per cent.

*Sodium Nitrate.*—Commercially pure specimen recrystallised and dried at 100°. 0.3641 gram of substance in about 5 c.c. of water precipitated with 1.3 grams of potassium salt, required 55.2 c.c. of permanganate (C). Na Found = 27.36 per cent., Calculated 27.05 per cent.

*Mixture of Sodium Chloride and Magnesium Sulphate.*—Magnesium sulphate gives no precipitate with potassium dihydroxytartrate. 0.2307 gram NaCl mixed with 0.3 gram  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$  dissolved in about 7 c.c. of water and precipitated with 0.8 gram of potassium salt, required 50.3 c.c. permanganate (C). Na Found = 39.35 per cent., Calculated 39.31 per cent.

The presence of magnesium, therefore, does not interfere with the accuracy of the sodium estimation.

*Mixture of Sodium Chloride and Ammonium Chloride.*—0.3225 gram NaCl mixed with 0.4 gram  $\text{NH}_4\text{Cl}$  dissolved in about 8 c.c. of water and precipitated with 1.1 grams of potassium salt, required 67.95 c.c. of permanganate (C). Na Found = 38.03 per cent., Calculated 39.31 per cent.

From this result, it would appear that the presence of excess of ammonium salt tends to give low results in the sodium value.

*Rochelle Salt.*—Commercially pure specimen: pressed. 1.2569 gram of substance precipitated with 1.2 grams of potassium salt, required 54.85 c.c. of permanganate (C). Na Found = 7.87 per cent., Calculated 8.15 per cent.

Sodium salts of weak acids whose solutions give an alkaline reaction



with litmus, such as phosphate and acetate, give somewhat low results when precipitated by means of the potassium salt. But with *free* dihydroxytartaric acid, such salts give normal, or nearly normal, results. This is probably due to the instability of sodium dihydroxytartrate in presence of alkalis, a fact which was indicated in the low results obtained in presence of free ammonia, and in the action previously mentioned of sodium hydroxide (Trans., 1898, 73, 74).

Free dihydroxytartaric acid gives a precipitate with all sodium salts which have been examined, with the exception of the borate (see below). Even salts of strong acids, such as sulphate, chloride, and nitrate, are, on standing, partially precipitated, and in the case of weaker acids, the precipitation appears to be complete, or nearly so. It is possible that the relative avidities of many acids might be compared in this manner.

*Sodium Acetate.*—A commercially pure specimen recrystallised and pressed.

I. 0.4014 gram substance dissolved in 5 c.c. water and precipitated with 1.05 grams of *potassium salt*, required 36.65 c.c. of permanganate (C). Na Found = 16.48 per cent.

II. 0.6458 gram substance dissolved in 5 c.c. of water and precipitated with 0.5 gram of *free dihydroxytartaric acid* required 60.9 c.c. of permanganate (C). Na Found = 16.98 per cent., Calculated 16.91 per cent.

*Sodium Phosphate.*—A commercially pure specimen recrystallised and pressed.

I. 0.8664 gram substance dissolved in 10 c.c. of water and precipitated with 1.2 grams of *potassium salt*, required 58.4 c.c. of permanganate (C). Na Found = 12.16 per cent.

II. 1.0814 gram substance dissolved in 10 c.c. of water and precipitated with 1 gram of *free dihydroxytartaric acid* required 73.8 c.c. of permanganate (C). Na Found = 12.31 per cent., Calculated 12.84 per cent.

*Sodium Carbonate.*—This gives low results, even with the free acid. This is probably due to the difficulty of preventing loss by spirting without unnecessary dilution of the solution, by washing, and perhaps also to the difficulty of preventing a rise of temperature during neutralisation. With the potassium salt as precipitant, 38.68 per cent. Na was obtained, and with the free acid 42.85 per cent., theory requiring 43.43 per cent.

Carbonates should, therefore, be first acidified, say, by hydrochloric acid, with due precautions against loss by spirting, the solution evaporated to dryness, and the residue dissolved in a small quantity of water.]

*Borax.*—This salt is altogether exceptional in its behaviour, since its solution gives *no precipitate whatever*, either with the potassium

salt or with the free acid. In this respect, it differs from all other sodium salts which have been examined. The reason for this difference is under investigation. Possibly, as with some other hydroxy-acids (for example, tartaric and salicylic), a compound is formed, which is soluble in water. Boric acid, if present, must therefore be removed by one of the usual methods, such as by methylic alcohol and hydrogen chloride, before sodium is estimated.

*Directions for Working the Process.*

In order to ensure accurate results, attention must be given to the following details.

Metals other than potassium, sodium, and magnesium must be absent. (Possibly some other metals may prove to be admissible, but only a few have been examined. Ammonium salts, if present in any quantity, appear to produce low results, so had better be removed.)

The metals should be present preferably as chlorides, sulphates, or nitrates. The solution to be examined must be concentrated and neutral.

Potassium dihydroxytartrate,  $K_2(C_4H_4O_8) \cdot H_2O$ , is dissolved in the least quantity (about 30 times its weight) of ice-cold water. The salt dissolves with some difficulty, and the solution, if not completely clear, is filtered before use.

Both solutions having stood in melting ice for a few minutes, the potassium salt is added in excess, the mixture kept in melting ice for half an hour, with occasional stirring, and the precipitated sodium salt, after being collected on a small filter, is drained with the assistance of the pump, and quickly washed three or four times with small quantities (about 4 or 5 c.c.) of ice-cold water, draining each time. The precipitate is then dissolved off the filter with a large excess of dilute sulphuric acid, and the solution titrated with potassium permanganate at the ordinary temperature of the laboratory.

The permanganate may be standardised by the usual methods (by oxalic acid or ammonium oxalate) and the result calculated from the relation which is shown to exist between permanganate and dihydroxy-tartaric acid; but the simplest and best method is to standardise the permanganate indirectly by means of pure *sodium chloride*, proceeding exactly as above directed.

If salts of weak acids, which give an alkaline reaction, such as acetates or phosphates, are to be examined, the free acid should be substituted for the potassium salt. Carbonates or hydroxides must first be neutralised, and boric acid, if present, must be removed by one of the usual methods, such as by methylic alcohol and hydrogen chloride. The results obtained appear to be as accurate as can be expected from

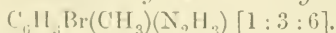
any volumetric process of the kind. The method could, of course, be varied in several ways. For instance, a measured excess of potassium dihydroxytartrate might be employed and the excess estimated after precipitation. Or the sodium salt could be determined gravimetrically by converting it into sulphate, chloride, &c., or it could be heated with water and the carbon dioxide estimated.

This volumetric process is probably much more economical than the estimation of potassium by platinum chloride; it is certainly very much more rapid, and probably quite as accurate, so that in the case of a mixture consisting entirely of potassium and sodium salts, where it is desired to estimate one of the metals only, it would be more advantageous to determine the sodium than the potassium.\*

### *Qualitative Detection of Sodium.*

In a former communication (Trans., 1895, 67, 48), the use of free dihydroxytartaric acid was proposed as a reagent for the detection of sodium, the solution to be examined being mixed with a solution of the acid, neutralised with ammonia, and the mixture stirred, preferably on a watch-glass. The *potassium salt*, however, affords a far more convenient reagent, since the necessity for neutralisation is dispensed with, and the introduction of ammonia is avoided; it was shown above that the presence of ammonia and of ammonium salts tended to give low results in the sodium value, so that for qualitative detection of small quantities its presence is objectionable. By using ice-cold solutions of the potassium salt and of the substance to be examined, and keeping the mixture for some time at 0°, it is fairly easy to detect one part of sodium in over 2000 parts of water.

## XII.—*Derivatives of Bromotolylhydrazine,*



By J. T. HEWITT, M.A., D.Sc., Ph.D., and F. G. POPE.

SEVERAL years ago, one of the authors described orthochlorophenylhydrazine and several of its derivatives (Trans., 1891, 59, 209; 1893, 63, 868). It was hoped that, under certain conditions, some of the

\* Wishing to test the working of the process in other hands, I asked one of our students, Mr. H. Jackson, of Downing College, to determine the sodium in a sample of pure sodium chloride.

Proceeding according to the instructions given above, and using the permanganate solution C, he obtained the following result: 0.2765 gram substance required 60.2 c.c. of permanganate. Na found = 39.29 per cent., Calculated 39.31 per cent.

derivatives of this hydrazine might lose hydrogen from the side chain and halogen from the nucleus, forming closed ring compounds, but no results of any value in this direction were obtained, and the problem remained as to whether bromine compounds might not be more suitable for such syntheses. Orthobromaniline, however, is comparatively difficult to obtain pure, whereas orthobromoparatoluidine can be prepared in any quantity by Wroblewsky's method (*Annalen*, 1873, 168, 153). The paratoluidine is first converted into acetoparatoluidide, the finely-powdered crude product (105 grams) is mixed with a large excess of cold water (1 litre), and the calculated amount of bromine (116 grams) run slowly into the mixture with continual stirring; the mixture is now raised to boiling, allowed to cool, and the supernatant liquor run off the cake of orthobromacetoparatoluidide. The hydrolysis is readily effected by boiling the product with five times its weight of hydrochloric acid (2 vols. HCl:1 water); on cooling, the hydrochloride of orthobromoparatoluidine separates out almost completely, and may be recrystallised from hot dilute hydrochloric acid.

This hydrochloride is converted into the corresponding hydrazine hydrochloride by the methods proposed by Victor Meyer and Lecco (*Ber.*, 1883, 16, 2976) and by Bamberger (*Ber.*, 1896, 29, 1834); but as the former method gives better yields, we have used it exclusively. It is preferable to work with small quantities at a time. The finely powdered orthobromoparatoluidine hydrochloride (22.25 grams), mixed with 10 times its weight of fuming hydrochloric acid, and cooled by ice and salt, is diazotised by the gradual addition of sodium nitrite (7 grams) dissolved in water (30 c.c.); after being left for 1 hour in the freezing mixture, it is poured, with continual stirring, into a solution of stannous chloride (37.8 grams) in its own weight of fuming hydrochloric acid kept well below 0°. During conversion of the diazonium into hydrazine salt, it is necessary to keep the temperature low, and it is advisable to pour the diazo-solution into the stannous chloride, otherwise the heat developed is liable to decompose the diazonium salt, with production of tarry products. The double tin salt of the hydrazine obtained is collected, and after drying on porous tiles, is dissolved in boiling water and freed from tin by hydrogen sulphide; on concentrating the clear solution, the hydrazine hydrochloride is deposited in colourless needles.

An aqueous solution of this salt shows the characteristic reduction of Fehling's solution.

Analysis. —  $C_7H_6Br \cdot NH \cdot NH_2 \cdot HCl$  requires N = 11.79 per cent. Found N = 11.51.

The purified salt melts at 190° with slight evolution of gas. The free hydrazine can readily be obtained by precipitating a solution of

the hydrochloride with ammonia; after recrystallisation from ether, it is obtained in beautiful, colourless, silky needles melting at  $91^{\circ}$ .

Analysis.— $C_7H_6Br \cdot NH \cdot NH_2$  requires  $N = 13.93$  per cent. Found  $N = 13.96$  per cent.

Salts of the hydrazine were prepared by dissolving it in ether, and adding ethereal solutions of the corresponding acids.

The *nitrate* separates from the ethereal solution in radiating masses, so that the liquid is soon filled with a paste of crystals, white and pearly in appearance; after being dried on a porous tile, they melt at  $154^{\circ}$  with slight decomposition.

Analysis.— $C_7H_6Br \cdot NH \cdot NH_2 \cdot HNO_3$  requires  $N = 15.91$  per cent. Found  $N = 15.29$  per cent.

*Sulphate*.—This was prepared in a similar manner, but an excess of acid had to be avoided or the sulphate and excess of acid separated as a heavy oily layer. By recrystallisation from boiling water, the sulphate was obtained in long, colourless needles easily soluble in hot, but only sparingly in cold, water, and melting at  $201^{\circ}$ .

Analysis.— $(C_7H_6Br \cdot N_2H_3)_2 \cdot H_2SO_4$  requires  $SO_4 = 19.20$  per cent. Found  $SO_4 = 19.22$  per cent.

The *oxalate* was immediately precipitated as a colourless, crystalline paste on mixing ethereal solutions of the hydrazine and anhydrous oxalic acid; the product was collected, dried on a tile, and recrystallised from boiling water, in which it dissolves fairly when hot, but only very slightly when cold. It separates in small, colourless prisms soluble in hot alcohol, and melting at about  $150^{\circ}$ , the exact temperature depending on the rate of heating; decomposition takes place apparently, the molten mass frothing, although it still remains colourless, so that probably the reaction consists in the formation of a hydrazide.

Analysis.— $(C_7H_6Br \cdot N_2H_3)_2 \cdot C_2O_4H_2$  requires  $N = 11.39$  per cent. Found  $N = 11.64$  per cent.

Besides the above salts, we have characterised the hydrazine by converting it into a number of derivatives.

*Acetyl bromotolylhydrazine* was prepared by boiling the hydrazine with excess of glacial acetic acid for some hours in a reflux apparatus; the product was then poured into water, collected, and recrystallised twice from dilute acetic acid. It forms small, thick prisms melting at  $124^{\circ}$ . The composition was confirmed by a nitrogen estimation.

Analysis.— $C_7H_6Br \cdot NH \cdot NH \cdot CO \cdot CH_3$  requires  $N = 11.53$  per cent. Found  $N = 11.77$  per cent.



This acetyl derivative dissolves slightly in hot, but is practically insoluble in cold, water; it is also insoluble in light petroleum, and in benzene and its homologues. It is taken up sparingly by ether, dissolves in alcohol and glacial acetic acid, and is dissolved with great readiness by chloroform.

*Bromotolylsemicarbazide* was immediately precipitated on mixing aqueous solutions of the hydrazine hydrochloride, and potassium cyanate in molecular proportion. It was collected, washed with cold water, and recrystallised from a large quantity of boiling water, in which it is only sparingly soluble; it is nearly insoluble in cold water.

Analysis.— $C_7H_6Br \cdot NH \cdot NH \cdot CO \cdot NH_2$  requires  $N = 17.21$  per cent. Found  $N = 17.14$  per cent.

This semicarbazide is insoluble in light petroleum and benzene; dissolves somewhat in chloroform, and is readily soluble in ether, acetone, and glacial acetic acid. It melts at  $163^\circ$ .

*Bromotolylallylthiosemicarbazide* was obtained by mixing ethereal solutions of allylthiocarbimide and the hydrazine in molecular proportion; on evaporating the ether, the thiosemicarbazide was left as an oil, which, on long continued stirring, solidified to a hard mass. On recrystallisation from alcohol, it was obtained in colourless prisms, the faces of which are often striated, the prisms themselves being frequently united in clusters. The ends of the prisms were usually badly developed.

A sulphur estimation gave  $S = 11.55$  per cent.  $C_7H_6Br \cdot NH \cdot NH \cdot CS \cdot NH \cdot C_3H_5$  requires  $S = 11.23$  per cent.

This semicarbazide melted at  $136.5^\circ$ , and showed no signs of the isomerism observed by Marekwald in compounds of a similar type. It dissolves in alcohol, ether, ethylic acetate, acetone, benzene, carbon bisulphide, and glacial acetic acid, but is insoluble in light petroleum. On adding copper sulphate solution to the ethereal solution, the latter becomes yellow, and turns a very dark olive brown on adding ammonia.

*Bromotolylphenylthiosemicarbazide* was obtained in like manner, using ethereal solutions of the hydrazine and phenylthiocarbimide. On evaporating the ether, an oil was left which solidified on stirring it up with a small quantity of light petroleum. Dried on a porous tile, it melted almost completely about  $122$ – $125^\circ$ , but after crystallisation from hot alcohol and drying at  $100^\circ$ , the melting point was found to be  $142^\circ$ . The substance, when somewhat rapidly deposited from alcohol, forms tufts of prisms, whilst by slower evaporation the prisms are obtained singly and are all terminated with well-defined oblique faces.

Analysis.— $C_7H_6Br \cdot NH \cdot NH \cdot CS \cdot NH \cdot C_6H_5$  requires  $S = 9.52$ ;  $Br = 23.81$  per cent. Found  $S = 9.55$ ;  $Br = 22.63$  per cent.

As to whether the above-mentioned behaviour of the substance on heating is to be ascribed to isomerism in the sense indicated by Marckwald (*Ber.*, 1892, 25, 3098) in the case of diphenylthiosemicarbazide, we cannot say; it is, however, strange that, on mixing solutions of pure hydrazine and allyl- or phenyl-thiocarbimide and evaporating, the respective thiosemicarbazides should be obtained as viscous liquids which do not readily solidify.

The substance is easily soluble in cold chloroform and acetone, and in warm alcohol, and fairly so in ether; but benzene, toluene, xylene or amyl alcohol take it up easily. It does not dissolve very easily in concentrated sulphuric acid, and in ammonia, even if warm and concentrated, but very sparingly, if at all. Warm dilute soda solution takes it up easily, but it is reprecipitated by hydrochloric acid. The thiosemicarbazide is turned superficially red by the vapour of fuming nitric acid; in actual contact with the fuming acid, it catches fire.

*Furfuraldehydebromotolylhydrazone*.—Furfuraldehyde (1 gram) in a small bottle, was covered with water, and a solution of the hydrazine hydrochloride (2.5 grams) added; on adding a solution of sodium acetate, the hydrazone was precipitated as an oil which obstinately refused to solidify, but after a month it became nearly solid, and on washing with a little alcohol and stirring, complete solidification was induced. When slowly crystallised from warm alcohol, it was deposited in well-defined, brown needles which melted at 87°.

Analysis.— $C_4H_3O \cdot CH:N \cdot NH \cdot C_7H_6Br$  requires N = 10.03 per cent. Found N = 9.77 per cent.

Furfuraldehydebromotolylhydrazone dissolves easily in ether, ethylic acetate, chloroform, acetone, and glacial acetic acid, but is insoluble in light petroleum.

*Benzaldehydebromotolylhydrazone*, prepared in a similar manner, separated at first as a pale yellow oil, which, however, on vigorous shaking, was suddenly transformed to a nearly colourless, crystalline mass; by recrystallisation from alcohol, it was obtained in well-defined, colourless, rhomboidal plates which melted at 84°; the alcoholic solution frequently shows the phenomenon of supercooling. Benzaldehydetolylhydrazone dissolves in ether, chloroform, ethylic acetate, benzene, and glacial acetic acid, but is insoluble in light petroleum.

Analysis.— $C_6H_5 \cdot CH:N \cdot NH \cdot C_7H_6Br$  requires N = 9.69 per cent. Found N = 10.11 per cent.

*Salicylaldehydebromotolylhydrazone*.—The free hydrazine liberated from 4 grains of the hydrochloride by 2 grams of sodium acetate was collected, washed, and dissolved in alcohol; on adding the calculated quantity (2 grams) of salicylaldehyde, a brownish oil separated imme-

diately, and this, after the supernatant liquid had been removed, became solid on stirring vigorously with some light petroleum. The crystalline mass, after being washed with light petroleum and recrystallised successively from ether and alcohol, was obtained in long, straw-coloured needles which melted at  $109^{\circ}$ .

Analysis.— $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{N}\cdot\text{NH}\cdot\text{C}_7\text{H}_6\text{Br}$  requires  $\text{N} = 9.18$  per cent. Found  $\text{N} = 9.08$  per cent.

The salicylaldehydehydrazone dissolves in ether, acetone, chloroform, ethylic acetate, carbon bisulphide, benzene, and glacial acetic acid, but only sparingly in alcohol, and is insoluble in light petroleum.

*Pyruvic acid bromotolylhydrazone* is completely precipitated by mixing aqueous solutions of the hydrazine hydrochloride and pyruvic acid; the pale yellow flocks thus formed, after being washed and recrystallised from hot dilute alcohol, are obtained in bright yellow crystals which melt at  $175^{\circ}$  to a clear yellow liquid, some gas being evolved. The substance is soluble in chloroform, ether, acetone and glacial acetic acid, but insoluble in benzene and light petroleum.

Analysis.— $\text{C}_7\text{H}_6\text{Br}\cdot\text{NH}\cdot\text{N}\cdot\text{C}(\text{CH}_3)\cdot\text{COOH}$  requires  $\text{C} = 44.28$ ;  $\text{H} = 4.06$  per cent. Found  $\text{C} = 44.30$ ;  $\text{H} = 4.09$  per cent.

*Ethylic pyruvate bromotolylhydrazone* was prepared by boiling the acid for 2 hours with an equal weight of concentrated sulphuric acid and 10 times its weight of alcohol, using a reflux apparatus. The mixture was then poured into a dilute solution of sodium carbonate, allowed to stand overnight, and the substance collected, washed, and dissolved in alcohol; on allowing the solution to evaporate slowly, the compound was deposited as tufts of slightly yellowish needles.

Analysis.— $\text{C}_7\text{H}_6\text{Br}\cdot\text{NH}\cdot\text{N}\cdot\text{C}(\text{CH}_3)\cdot\text{COOC}_2\text{H}_5$  requires  $\text{N} = 9.36$  per cent. Found  $\text{N} = 9.83$  per cent.

It softens about  $75^{\circ}$  and melts at  $84\text{--}85^{\circ}$ . It is easily soluble in the usual solvents.

Various salts of this acid were prepared, in the hope of eliminating the metal in union with bromine, on heating, and so possibly obtaining closed ring derivatives. As the experiments in this direction have not as yet yielded very satisfactory results, we have decided to publish the remainder of our work now, and leave this portion for a future communication.

The *potassium salt* was prepared by mixing the acid with the calculated quantity of pure anhydrous potassium carbonate, adding water, and warming until the evolution of carbon dioxide had ceased. Enough water was then added to dissolve all the salt on boiling, and the solution, filtered hot, was allowed to cool; the salt then separated in

fern-like aggregates, which were collected with the aid of the pump, washed with alcohol, and air-dried.

Analysis.— $C_7H_6Br \cdot NH \cdot N : C(CH_3) \cdot COOK + 3H_2O$  requires  $H_2O = 14.60$  ;  $K = 10.74$  per cent. Found  $H_2O = 14.56$  ;  $K = 10.33$  per cent.

The *ammonium salt* was obtained by dissolving the acid in hot dilute ammonia ; the crystals deposited on cooling are, like those of the potassium salt, not very soluble in cold water.

Analysis.— $C_7H_6Br \cdot NH \cdot N : C(CH_3) \cdot COONH_4$  requires  $N = 14.58$  per cent. Found  $N = 14.40$  per cent.

The aqueous solution of this salt gives precipitates with solutions of salts of the heavy metals. The precipitate with silver nitrate becomes violet coloured on drying, and decomposes readily on heating. The analysis of the dried salt showed that considerable decomposition had taken place, it contained 34.56 per cent. of silver, whilst the salt  $C_{10}H_{10}BrN_2O_2Ag$  should contain 28.57 per cent.

The *lead salt* is a pale yellow, amorphous powder ; dried at  $105^\circ$ , it gave a percentage of lead agreeing with the theoretical numbers.

Analysis.— $[C_7H_6Br \cdot NH \cdot N : C(CH_3)COO]_2Pb$  requires  $Pb = 27.71$  per cent. Found  $Pb = 28.05$  per cent.

*Action of Heat on these Salts.*—The anhydrous potassium salt, when heated gradually, remains unchanged below  $215^\circ$ , but at this temperature, a brisk reaction takes place, the salt melts, the mass darkens and froths up, and small quantities of liquid distil up the sides of the tube. On cooling and extracting the melt with hot water, the aqueous solution was found to contain potassium bromide ; the insoluble portion yields extracts both with dilute hydrochloric acid and dilute soda. It is thus seen that both a basic and acidic (or at least phenolic) substance are formed during the change ; their nature has, however, not yet been determined.

The lead salt decomposes at about  $160^\circ$  or  $170^\circ$ . Much lead bromide is formed, and again both acid and basic products can be detected. A similar decomposition takes place, and apparently more smoothly, by heating the lead salt with an indifferent hydrocarbon solvent for some hours in sealed tubes at  $180^\circ$ .

We hope to shortly return to this subject, and lay the results obtained before the Society.

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### XIII.—*Effect of the Mono-, Di-, and Tri-chloroacetyl Groups on the Rotatory Power of Methylic and Ethylic Glycerates and Tartrates.*

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Late Priestley Scholar in Mason University College, Birmingham.

THE effect of attaching halogens to the asymmetric carbon-atom has been the subject of numerous researches in which chlorine or bromine is substituted for the hydroxyl group of an optically active compound. In the earlier investigations of this nature, the substitution was effected by the action of the halogen acid, with the result that the halogen compound obtained was invariably inactive. Thus, from *l*-malic acid and hydrobromic acid, Kekulé (*Ann.*, 1864, 130, 25) obtained only inactive bromosuccinic acid; from *l*-mandelic acid and hydrochloric and hydrobromic acids, Easterfield (*Trans.*, 1891, 59, 71) obtained only inactive chloro- and bromo-phenylacetic acids; similarly, from active (*l* and *d*) isopropylphenylglycollic acids, Fileti (*J. pr. Chem.*, 1892, 46, 562), by the action of hydrochloric acid, obtained inactive isopropylphenylchloroacetic acid only. The uniformity of these results not unnaturally led to the impression that such introduction of the halogen atoms must necessarily be attended with racemisation, and even gave rise to a suspicion that possibly the mere difference in the four groups attached to the carbon atom was not in itself sufficient to cause optical activity (Hantzsch, *Grundriss d. Stereochemie*). The incorrectness of these views has been more recently demonstrated by Le Bel (*Bull. soc. chim.*, [iii], 1893, 9, 674), and more especially by Walden (*Ber.*, 1895, 28, 1297), who, by acting with the halogen compounds of phosphorus on the ethereal salts of malic, tartaric, lactic, and mandelic acids, has obtained active ethereal salts of bromosuccinic, bromomalic, chloro- and bromopropionic, chloro- and bromo-phenylacetic acids, whilst these results have been further extended by J. Wallace Walker (*Trans.*, 1895, 67, 914) in respect of chloro- and bromo-propionic acid.

In the substitutions by chlorine and bromine referred to above, it is very noteworthy that the sign of the rotation is reversed by the introduction of the halogen, a result which is contrary to what takes place when substitution in the same compounds is made by most other groups. This circumstance led to the idea that there was something anomalous in the rotatory effect of the halogen atom attached to the asymmetric carbon atom. It has, however, been shown by Walden (*Ber.*, 1895, 28, 2766; 1896, 29, 133) that the change in sign in the case of the ethereal salts of *d*-chloro-



succinic acid obtained from the *l*-malic salt is due to a most remarkable transformation, for on regenerating malic acid from the *d*-chlorosuccinic acid, it is *d*-malic, and not *l*-malic, acid which is obtained, and a similar transformation has been shown to take place by Purdie and Williamson (Trans., 1896, 69, 837) in passing from the levorotatory lactic to the dextrorotatory chloropropionic ether, the latter, on removal of the halogen, yielding the dextrorotatory lactic compound. It is thus evident that the chloro- and bromo-compounds *really* corresponding to the tartaric, malic, and lactic compounds from which they are derivable, and in which the halogen is attached to the same bond of the asymmetric carbon atom as that to which the original hydroxyl group of the parent substance was united, have a rotatory power of the same sign as the particular parent substance in question.

The above results all refer to the effect of uniting the halogen directly to the asymmetric carbon atom, and at the time our experiments were commenced there existed, so far as we are aware, only a few isolated observations of Le Bel's (*loc. cit.*) and of Walden's on the rotatory effect of halogen-atoms not so directly attached. The following is the extent of the observations made by Le Bel on this subject.

Propylene glycol,  $\text{CH}_3 \cdot \text{CH}(\text{OH}) \cdot \text{CH}_2 \cdot \text{OH}$ ,  $\alpha = -1^\circ 57'$  ( $l = 22$  cm.).

Propylene glycol diacetate,  $\text{CH}_3 \cdot \text{CH}(\text{O} \cdot \text{C}_2\text{H}_3\text{O}) \cdot \text{CH}_2 \cdot \text{O} \cdot \text{C}_2\text{H}_3\text{O}$ ,  $\alpha = -8$  ( $l = 22$  cm.).

Propylene glycol monochlorhydrin,  $\alpha = -53'$  ( $l = 22$  cm.).

Propylene glycol dichlorhydrin,  $\alpha = -23'$  ( $l = 10$  cm.).

Propylene glycol chlorobromhydrin,  $\text{CH}_3 \cdot \text{CHBr} \cdot \text{CH}_2\text{Cl}$ ,  $\alpha = -38'$  ( $l = 10$  cm.).

Propylene glycol chloracetin,  $\text{CH}_3 \cdot \text{CH}(\text{O} \cdot \text{C}_2\text{H}_3\text{O}) \cdot \text{CH}_2\text{Cl}$ ,  $\alpha = +1^\circ 18'$  ( $l = 22$  cm.).

Propylene glycol chlorochloracetin,  $\text{CH}_3 \cdot \text{CH}(\text{C}_2\text{H}_2\text{ClO}_2) \cdot \text{CH}_2\text{Cl}$ ,  $\alpha = +49'$  ( $l = 10$  cm.).

Propylene glycol chlorobutyryn,  $\text{CH}_3 \cdot \text{CH}(\text{O} \cdot \text{CO} \cdot \text{C}_3\text{H}_7) \cdot \text{CH}_2\text{Cl}$ ,  $\alpha = +27'$  ( $l = 10$  cm.).

From the above it will be seen that propylene glycol chloracetin has nearly the same rotation as propylene glycol chlorochloracetin, so that in this case the substitution of chlorine for hydrogen at a point remote from the asymmetric carbon atom does not very materially affect the rotation.

The observations which had been made by Walden (*Zeit. physikal. Chem.*, 1895, 17, 264) referred to the rotation of some monochloracetyl- and monobromacetyl-malates, a full summary of which will be found in a paper by one of us (Trans., 1896, 69, 122).

Again, more recently still, since the work recorded in this paper

was performed, some compounds have been prepared by Guye and Chavanne (*Bull. soc. chim.*, [iii], 1896, 15, 177—195, 275—305) which have a bearing on the same subject.

Amylic alcohol .....	$[\alpha]_D^{16} = -4.52^\circ$	$[\alpha]_D^{76} = -4.12^\circ$
„ acetate .....	$[\alpha]_D^{20} = +2.53$	$[\alpha]_D^{57} = +2.51$
„ propionate .....	$[\alpha]_D^{20} = +2.77$	$[\alpha]_D^{67} = +2.68$
„ monochloracetate .....	$[\alpha]_D^{22} = +3.44$	$[\alpha]_D^{60} = +3.36$
„ dichloracetate .....	$[\alpha]_D^{22} = +2.77$	$[\alpha]_D^{60} = +2.65$
„ trichloracetate.....	$[\alpha]_D^{22} = +2.71$	$[\alpha]_D^{60} = +2.58$
„ monochloropropionate ...	$[\alpha]_D^{22} = +3.03$	

It was with the object of extending this knowledge of the rotatory effect of the halogen-substituted fatty acid radicles that our investigation was undertaken, but before its completion the results of a somewhat similar inquiry were published by Freundler (*Bull. soc. chim.*, [iii], 1895, 13, 1055), whose experiments are, however, limited to an examination of the methylic, ethylic, propylic, and isobutylic salts of dimonochloracetyl tartaric acid. Our investigations, therefore, only overlap in the matter of the preparation and study of two single compounds, to which special attention will be directed later on.

## I. TRICHLORACETYL DERIVATIVES.

*Preparation of Trichloroacetyl Chloride.*—This was effected by utilising Friedel's reaction in the manner described by Friederici (*Ber.*, 1878, 11, 1971). A mixture of 100 grams of trichloroacetic acid and 150 grams of phosphoric anhydride was heated at about  $200^\circ$  in a Wurtz flask of about 2 litres capacity and dry hydrogen chloride passed into the flask above the surface of the mixture. The lateral tube of the flask was connected with a U-tube surrounded with ice and provided with a tubulure below, passing into a small flask in which the condensed liquid was collected. Only slight charring took place, and a good yield of chloride was obtained, but the process is slow, two or three days being required for the preparation of 60—70 grams. The chloride was fractionated, using a Hempel tube, and was ultimately obtained almost entirely free from phosphorus compounds.

We adopted this method of preparation for all the three chloroacetyl chlorides in consequence of its being the only one which yielded a product very nearly free from phosphorus compounds.

*Ethylic Di-trichloroacetyl glycerate.*—This was prepared by allowing 16 grams of ethylic glycerate ( $a_D = -11.47^\circ$  in 100 mm. tube at  $12^\circ$ ) to drop slowly into 130 grams of trichloroacetyl chloride at  $100^\circ$ , the mixture being maintained at this temperature for about 2 hours, and frequently shaken, a method which was adopted in the preparation of nearly all the other ethereal salts described in this paper. The product was then

submitted to distillation under diminished pressure, the excess of trichloroacetyl chloride passing over at 45—50°, a first fraction was collected at 198° and a second at 198—205°. The first fraction was again treated with trichloroacetyl chloride, and on distilling as above a fraction was collected between 200° and 205°, and this was mixed with the 198—205° fraction of the first distillation. This mixture was then refractionated until the rotation of the product became practically constant. In this way, 9 grams of substance, boiling at 202° under about 15 mm. pressure, and with the oil-bath at 240°, were obtained. The following chlorine determinations were made by Carius' method.

1. 0.7466 gave 1.4976 AgCl. Cl = 49.65 per cent.

2. 0.5608 „ 1.1354 AgCl. Cl = 50.06 „

3. 0.5657 „ 1.1360 AgCl. Cl = 49.67 „

4. 0.5200 „ 1.0405 AgCl. Cl = 49.50 „

5. 0.5651 „ 1.1340 AgCl. Cl = 49.64 „

$C_9H_8O_6Cl_6$  requires Cl = 50.11 per cent.

The rotation was determined at the following temperatures.

*Rotation of Ethylic Di-trichloroacetyl-glycerate.*

Temp.	Observed rotation in 44 mm. tube.	Density compared with water at 4°.	$[\alpha]_D$	$[\delta]_D^*$
12.5°	-12.73°	1.5502	-18.66°	
98	-11.68	1.4438	-18.39	-176.6°
77	-11.89	1.4702	-18.38	-178.7
60	-12.08	1.4925	-18.39	-180.6
48	-12.19	1.5060	-18.39	-181.9
42.5	-12.28	1.5127	-18.40	-182.8
12.6	-12.66	1.5502	-18.56	-186.9

The density determinations actually made were

$d_{12^\circ/4^\circ} = 1.5502.$        $d_{60^\circ/4^\circ} = 1.4915.$        $d_{100^\circ/4^\circ} = 1.4413.$

*Methylic Di-trichloroacetyl-glycerate.*—Twenty grams of methylic glycerate ( $\alpha = -6.30^\circ$  in 100 mm. tube at 13.3°) were slowly added to an excess of trichloroacetyl chloride at 110°, the heating being continued for several hours. The excess of trichloroacetyl chloride was distilled off under diminished pressure, and a fraction (30 grams) passing over at 185—204° was repeatedly fractionated, when 9 grams of the methylic salt distilling at 199—200°, under about 15 mm. pressure, and with the oil-bath at 225°, were obtained. The chlorine in this was determined.

$$* [\delta]_D = \frac{\alpha}{l} \sqrt[3]{\frac{M}{D}}$$

1. 0.7007 gave 1.4557 AgCl. Cl = 51.40 per cent.
  2. 0.6275 „ 1.3087 AgCl. Cl = 51.59 „
- $C_8H_6O_6Cl_6$  requires Cl = 51.82 per cent.

The rotation was determined at the following temperatures.

*Rotation of Methyl Di-trichloroacetyl-glycerate.*

Temp.	Observed rotation in 44 mm. tube.	Density compared with water at 4°.	$[\alpha]_D$	$[\delta]_D$
11.5°	- 10.03°	1.6125	- 14.13°	- 144.5°
98.3	- 10.07	1.4964	- 15.29	- 148.8
12	- 10.05	1.6118	- 14.17	- 144.8

The density determinations actually made were

$$d_{117^\circ/4^\circ} = 1.6122, \quad d_{50^\circ/4^\circ} = 1.5582, \quad d_{100^\circ/4^\circ} = 1.4942.$$

*Ethyl Mono-trichloroacetyl-tartrate.*—Thirty grams of ethylic tartrate ( $a_D = +8.47^\circ$ ,  $t = 13^\circ$ ,  $l = 1$ ) and 200 grams of trichloroacetyl chloride, heated at  $120^\circ$  for 3 hours as before, were subsequently distilled under diminished pressure; the excess of trichloroacetyl chloride passed over first; at  $160^\circ$ , what appeared to be unaltered ethylic tartrate was collected, whilst the ethylic salt (40 grams) came over mostly at  $190^\circ$ . After two refractionations, the boiling point was  $195^\circ$  (oil bath  $230^\circ$ , pressure about 16 mm.), and as the rotation had hardly been affected by the last distillation, the chlorine was determined by Carius' method.

1. 0.5463 gave 0.6625 AgCl. Cl = 30.00 per cent.
2. 0.5486 „ 0.6635 AgCl. Cl = 29.92 „

The substance was then again twice redistilled, the boiling point being  $185^\circ$  (oil bath  $210^\circ$ , pressure about 16 mm.), and the final product again analysed.

1. 0.5804 gave 0.7050 AgCl. Cl = 30.05 per cent.
  2. 0.6782 „ 0.8220 AgCl. Cl = 29.98 „
- $C_{10}H_{13}O_7Cl_3$  requires Cl = 30.30 per cent.  
 $C_{12}H_{12}O_8Cl_6$  „ Cl = 42.48 „

The substance obtained was, therefore, ethylic mono-trichloroacetyl-tartrate.

With this, the following polarimetric observations were made.

*Rotation of Ethylic Mono-trichloroacetyl-tartrate.*

Temp.	Observed rotation in 44 mm. tube.	Density compared with water at 4°.	$[\alpha]_D$	$[\delta]_D$
11.6°	+ 9.37°	1.3963	+ 15.25°	+ 134.5°
98.5	+ 10.01	1.2981	+ 17.53	+ 147.2
58.2	+ 9.88	1.3446	+ 16.70	+ 143.6
46.2	+ 9.81	1.3609	+ 16.39	+ 142.0
38.5	+ 9.77	1.3744	+ 16.16	+ 140.9
12.0	+ 9.39	1.3959	+ 15.30	+ 134.8

The density determinations actually made were

$$d_{11^\circ/4^\circ} = 1.3970. \quad d_{50^\circ/4^\circ} = 1.3541. \quad d_{100^\circ/4^\circ} = 1.2964.$$

*Methylic Mono-trichloroacetyl-tartrate.*—Thirty grams of methylic tartrate ( $\alpha_D = +2.28^\circ$ ,  $t = 16^\circ$ ,  $l = 1$ ), and 150 grams of trichloroacetyl chloride, after heating at  $110^\circ$  for two days, on distillation as before, gave a fraction at  $180$ — $210^\circ$  which crystallised soon after cooling. The crystals, after treatment with water to remove any unaltered methylic tartrate, were pressed between filter paper and dissolved in toluene. This solution, after drying with calcium chloride, was allowed to crystallise, and the greater part of the substance remaining in solution was deposited on adding light petroleum: 21 grams of crystalline substance were obtained. On recrystallisation from xylene, the melting point was  $79$ — $80^\circ$ , and two Carius' determinations of the chlorine gave the following results.

- 0.4737 gave 0.6286 AgCl. Cl = 32.83 per cent.
- 0.5293 „ 0.7015 AgCl. Cl = 32.77 „  
 $C_8H_9O_7Cl_3$  requires Cl = 32.92 per cent.  
 $C_{10}H_8O_8Cl_6$  „ Cl = 45.42 „

The substance obtained was, therefore, methylic mono-trichloroacetyl-tartrate.

The crystals of which the above analyses were made were recrystallised from hot xylene; after washing with a little xylene, they were ground up, and the powder, washed several times by decantation with light petroleum, was collected and dried in a vacuum desiccator. Its melting point was found as before to be  $79$ — $80^\circ$ , and with it the following polarimetric observations were made.

*Rotation of Methylic Mono-trichloroacetyl-tartrate.*

Temp.	Observed rotation in 44 mm. tube.	Density compared with water at 4°.	$[\alpha]_D$	$[\delta]_D$
100°	+ 6.29°	1.4081	+ 10.15°	+ 87.55°
62	+ 5.92	1.4536	+ 9.25	+ 81.53
51.5	+ 5.77	1.4667	+ 8.94	+ 79.23
17	+ 5.50	1.5083	+ 8.29	+ 74.82



The density terminations actually made were

$$\begin{array}{ll} d\ 17^{\circ}/4^{\circ} = 1.5083. & d\ 18^{\circ}/4^{\circ} = 1.5056. \\ d\ 50^{\circ}/4^{\circ} = 1.4686. & d\ 100^{\circ}/4^{\circ} = 1.4081. \end{array}$$

## II. DICHLORACETYL DERIVATIVES.

*Preparation of Dichloroacetyl Chloride.*—This was prepared by passing dry hydrogen chloride over a heated mixture of 100 grams of dichloroacetic acid and 150 grams of phosphoric anhydride. The action proceeds readily, the product being more rapidly obtained than in the case of the trichloroacetyl compound; there is, however, a considerable amount of charring and a quantity of gas, consisting almost exclusively of carbonic oxide, is given off.\* A good yield was obtained.

*Ethyllic Di-dichloroacetyl glycerate.*—This was prepared in the usual way from 28 grams of ethylic glycerate ( $\alpha_D = -11.40^{\circ}$ ,  $t = 23^{\circ}$ ,  $l = 1$ ) and 200 grams of dichloroacetyl chloride heated at  $106^{\circ}$  for two days, and then repeatedly fractionating. The crude product was washed with a warm solution of sodium carbonate, and extracted with benzene. The benzene solution was again washed with sodium carbonate, then several times with water, and after drying with calcium chloride, the benzene was first distilled off under atmospheric pressure, the residue being distilled under diminished pressure. The final product (7 grams) thus obtained distilled at  $203^{\circ}$  (oil bath at  $250^{\circ}$ , and under about 15 mm. pressure). The chlorine was determined by the Carius-Volhardt method. (Walker and Henderson, *Chem. News*, 71, 103, 295).

1. 0.2228 required 0.4236  $\text{AgNO}_3$ . Cl = 39.71 per cent.

2. 0.1588 „ 0.3011  $\text{AgNO}_3$ . Cl = 39.60 „

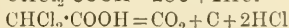
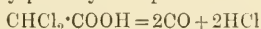
$\text{C}_9\text{H}_{10}\text{O}_6\text{Cl}_4$  requires Cl = 39.89 per cent.

The following polarimetric observations were made.

### *Rotation of Ethyllic Di-dichloroacetyl glycerate.*

Temp.	Observed rotation in 44 mm. tube.	Density compared with water at $4^{\circ}$	$[\alpha]_D$	$[\delta]_D$
$16.8^{\circ}$	$-11.82^{\circ}$	1.4667	$-18.32^{\circ}$	$-167.6^{\circ}$
35.1	$-12.17$	1.4446	$-19.15$	$-173.4$
46.5	$-12.31$	1.4291	$-19.58$	$-176.0$
59.7	$-12.41$	1.4129	$-19.96$	$-178.1$
99	$-12.66$	1.3669	$-21.05$	$-183.7$
16.8	$-11.83$	1.4667	$-18.33$	$-167.6$

\* The decomposition may possibly be represented thus



In this connection, it may be mentioned that Maumené (*Annalen*, 1865, 133, 154) has shown that the silver salt, on heating, decomposes into carbonic oxide, carbonic anhydride, and silver chloride.

The density determinations actually made were

$$\begin{aligned} d\ 16.8^\circ/4^\circ &= 1.4667. & d\ 31.5^\circ/4^\circ &= 1.4485. & d\ 46.5^\circ/4^\circ &= 1.4291. \\ d\ 59.7^\circ/4^\circ &= 1.4129. & d\ 100^\circ/4^\circ &= 1.3657. \end{aligned}$$

*Methylic Di-dichloroacetyl-glycerate*.—Fifteen grams of methylic glycerate ( $a_D = -6.44^\circ$ ,  $t = 16.5^\circ$ ,  $l = 1$ ) and 170 grams of dichloroacetyl chloride, heated at  $110^\circ$  for three days, were distilled as before, and passed over chiefly (30 grams) at  $200$ — $210^\circ$ . This distillate was shaken up with a warm solution of sodium carbonate and extracted with benzene, and the benzene solution was again washed with sodium carbonate solution and then with water; after drying with calcium chloride, the benzene was distilled off under atmospheric pressure, and the residue under diminished pressure. On repeated fractionation, which did not appreciably affect the rotation, the final product passed over at  $207^\circ$  (oil bath  $260^\circ$ , 20 mm. pressure). The chlorine was determined by the Carius-Volhardt method.

1. 0.3515 required 0.6942  $\text{AgNO}_3$ . Cl = 41.24 per cent.
  2. 0.3894     ,,     0.7672  $\text{AgNO}_3$ . Cl = 41.14     ,,
- $\text{C}_8\text{H}_8\text{O}_6\text{Cl}_4$  requires Cl = 41.52 per cent.

The following polarimetric observations were made.

*Rotation of Methylic Di-dichloroacetyl-glycerate.*

Temp.	Observed rotation in 44 mm. tube.	Density compared with water at $4^\circ$ .	$[\alpha]_D$	$[\delta]_D$
$15^\circ$	$-9.39^\circ$	1.5290	$-13.96^\circ$	$-129.6^\circ$
100	$-10.76$	1.4235	$-17.18$	$-152.0$
$74.4$	$-10.53$	1.4553	$-16.44$	$-147.9$
55	$-10.32$	1.4796	$-15.85$	$-143.9$
40	$-10.05$	1.4982	$-15.25$	$-139.6$
$14.5$	$-9.39$			

The density determinations actually made were

$$\begin{aligned} d\ 20^\circ/4^\circ &= 1.5228. & d\ 40^\circ/4^\circ &= 1.4982. & d\ 60^\circ/4^\circ &= 1.4734. \\ d\ 80^\circ/4^\circ &= 1.4484. & d\ 100^\circ/4^\circ &= 1.4235. \end{aligned}$$

*Ethylic Di-dichloroacetyl-tartrate*.—Thirty grams of ethylic tartrate ( $a_D = +9.31^\circ$ ,  $t = 20^\circ$ ,  $l = 1$ ) and 180 grams of dichloroacetyl chloride, heated at  $110^\circ$  for three days, gave a product the chief portion of which, on fractionation, passed over at  $220$ — $230^\circ$  (oil bath  $260^\circ$ , 20 mm. pressure). The yield was 35 grams.

This was shaken with a hot solution of sodium carbonate and extracted with benzene, &c., as in the preparation of the corresponding

glycerate (*q.v.*). The product, redistilled until the rotation was constant, boiled at  $225^{\circ}$  (oil bath  $260^{\circ}$ , about 15 mm. pressure).

The chlorine was determined by the Carius-Volhard method.

1. 0.1685 required 0.2648  $\text{AgNO}_3$ . Cl = 32.82 per cent.

2. 0.1681 „ 0.2625  $\text{AgNO}_3$ . Cl = 32.61 „

$\text{C}_{12}\text{H}_{14}\text{O}_8\text{Cl}_4$  requires Cl = 33.18 per cent.

The following polarimetric observations were made.

*Rotation of Ethylic Di-dichloroacetyltartrate.*

Temp.	Observed rotation in 92.35 mm. tube.	Density compared with water at $4^{\circ}$ .	$[\alpha]_D$	$[\delta]_D$
$16^{\circ}$	+ 21.28°	1.4137	+ 16.30°	+ 154.7°
41.5	+ 21.07	1.3845	+ 16.48	+ 154.2
54.7	+ 20.92	1.3695	+ 16.54	+ 153.7
74	+ 20.92	1.3468	+ 16.82	+ 154.5
100	+ 20.78	1.3171	+ 17.08	+ 154.7

The density determinations actually made were

$d\ 21^{\circ}/4^{\circ} = 1.4080$ .  $d\ 40^{\circ}/4^{\circ} = 1.3862$ .  $d\ 60^{\circ}/4^{\circ} = 1.3635$ .

$d\ 80^{\circ}/4^{\circ} = 1.3397$ .  $d\ 100^{\circ}/4^{\circ} = 1.3171$ .

*Methylic Di-dichloroacetyltartrate.*—Thirty grams of methylic tartrate ( $\alpha_D = +4.57$ ,  $t = 16^{\circ}$ ,  $l = 2$ ) and 150 grams of dichloroacetyl chloride, were heated at  $110^{\circ}$  for two days, and the product fractionated as before; the excess of acid chloride came over at about  $50^{\circ}$ , and the methylic salt between  $170$ — $220^{\circ}$ , chiefly at  $180^{\circ}$  (oil bath at  $215$ — $250^{\circ}$ ). On refractionating twice, some of the distillate crystallised spontaneously, and crystallisation was induced in the remainder by stirring with water. The solid was purified by trituration with a solution of sodium carbonate, drying on porcelain, and recrystallisation from xylene, the crystals being washed with a little xylene and then with light petroleum. The melting point was  $63.5$ — $64^{\circ}$ . A further quantity was recovered from the xylene solution by precipitation with light petroleum, the total amount being 8 grams. This was distilled, the boiling point being  $220$ — $221^{\circ}$  (oil bath  $260^{\circ}$ , about 15 mm. pressure), and the distillate, which rapidly solidified, melted at  $64$ — $65^{\circ}$ .

The chlorine was determined by the Carius-Volhard method.

1. 0.2243 required 0.3801  $\text{AgNO}_3$ . Cl = 35.39 per cent.

2. 0.2427 „ 0.4117  $\text{AgNO}_3$ . Cl = 35.42 „

$\text{C}_{10}\text{H}_{10}\text{O}_8\text{Cl}_4$  requires Cl = 35.50 per cent.

The following polarimetric observations were made.

*Rotation of Methyllic Di-dichloroacetyl tartrate.*

Temp.	Observed rotation in 44 mm. tube.	Density compared with water at 4°.	$[\alpha]_D$	$[\delta]_D$
19.2°	+ 7.93°	1.5056	+ 11.97°	+ 115.9°
37.6	+ 7.47	1.4827	+ 11.45	+ 109.7
48.2	+ 7.26	1.4693	+ 11.23	+ 106.9
55.2	+ 7.16	1.46065	+ 11.14	+ 105.7
98.5	+ 6.80	1.4101	+ 10.96	+ 101.8

The density determinations actually made were

$$d\ 19^\circ/4^\circ = 1.5058. \quad d\ 54^\circ/4^\circ = 1.4620. \quad d\ 100^\circ/4^\circ = 1.4083.$$

## III. MONOCHLORACETYL DERIVATIVES.

*Preparation of Monochloroacetyl Chloride.*—Considerably greater difficulty was encountered in the preparation of this than in the case of either the di- or tri-chloroacetyl chlorides, owing to the very large amount of charring which takes place when monochloroacetic acid is heated with phosphoric anhydride.

The method ultimately adopted consisted in introducing into a Wurtz flask, of 2 litres capacity, 150 grams of phosphoric anhydride, followed by 100 grams of melted monochloroacetic acid. The flask containing the mixture was then at once heated in an oil bath to about 200°, a rapid current of dry hydrogen chloride being passed through. The principal source of danger is the choking up of the lateral tube by the charred mass, which has a tendency to become extremely voluminous. In one experiment, 83 grams of crude chloride were obtained from 100 grams of the acid. The chloride was fractionated by means of a Hempel tube, and, after one distillation, was almost entirely free from phosphorus.

We may mention that we avoided the ordinary methods of preparing monochloroacetyl chloride, because, firstly, the chlorination of chloroacetyl chloride might lead to the formation of some dichloroacetyl chloride, and, secondly, the method of acting with the chlorides of phosphorus on monochloroacetic acid yields a product containing phosphorus compounds, which we were unable to remove by any available means. Instead of monochloroacetyl chloride, we tried, however, the use of monochloroacetyl bromide for acting on ethylic glycerate, but obtained an ethereal salt containing some bromine, and this method was, therefore, abandoned.

*Ethylic Di-monochloroacetyl glycerate.*—Seventeen grams of ethylic glycerate ( $\alpha_D = -11.49^\circ$ ,  $t = 14.5^\circ$ ,  $l = 1$ ) and 90 grams of monochloroacetyl chloride were heated at 110° for two days. On fractionating, the principal product came over at 200—205° (oil bath 235°, pressure

about 18 mm.); this was twice refractionated, the rotation being practically unaffected by the last distillation. The final product distilled at  $198^{\circ}$  (oil bath  $235^{\circ}$ , pressure about 15 mm.).

The chlorine was determined by the Carius-Volhardt method.

1. 0.1700 required 0.2058  $\text{AgNO}_3$ .  $\text{Cl} = 25.28$  per cent.

2. 0.2034 „ 0.2464  $\text{AgNO}_3$ .  $\text{Cl} = 25.29$  „

3. 0.5123 gave 0.5246  $\text{AgCl}$  (gravim.).  $\text{Cl} = 25.33$  „

$\text{C}_9\text{H}_{12}\text{O}_6\text{Cl}_2$  requires  $\text{Cl} = 24.74$  per cent.

The following polarimetric observations were made.

*Rotation of Ethylic Di-monochloroacetyl-glycerate.*

Temp.	Observed rotation in 44 mm. tube.	Density compared with water at $4^{\circ}$ .	$[\alpha]_D$	$[\delta]_D$
$100^{\circ}$	$-12.34^{\circ}$	1.2704	$-22.08^{\circ}$	$-170.8^{\circ}$
66	$-11.82$	1.3089	$-20.52$	$-162.0$
40	$-11.13$	1.3402	$-18.87$	$-151.4$
15	$-10.12$	1.3693	$-16.80$	$-136.6$

The density determinations actually made were

$$d\ 16^{\circ}/4^{\circ} = 1.3681.$$

$$d\ 50^{\circ}/4^{\circ} = 1.3279.$$

$$d\ 80^{\circ}/4^{\circ} = 1.2922.$$

$$d\ 100^{\circ}/4^{\circ} = 1.2704.$$

*Methylic Di-monochloroacetyl-glycerate.*—The methylic glycerate used was derived from 35 grams of crystallised calcium glycerate. The rotation of the methylic salt was  $a_D = -6.24^{\circ}$ ,  $t = 14.5^{\circ}$ ,  $l = 1$ .

This methylic glycerate was heated at  $110^{\circ}$  with 80—90 grams of monochloroacetyl chloride for two days. On fractionating the mixture, 21 grams of product were obtained boiling at  $190$ — $205^{\circ}$  (oil bath  $230^{\circ}$ , pressure about 15 mm.); this was successively washed with solution of sodium carbonate and with water, extracted with benzene, &c. (see p. 187). On fractionation, the main portion passed over at  $197^{\circ}$  (oil bath  $235^{\circ}$ , pressure about 15 mm.). This, when redistilled, exhibited the same boiling point and practically the same rotation.

The chlorine was determined by the Carius-Volhardt method.

1. 0.2044 required 0.2570  $\text{AgNO}_3$ .  $\text{Cl} = 26.26$ .

2. 0.5623 gave 0.5977  $\text{AgCl}$  (gravim.).  $\text{Cl} = 26.30$ .

$\text{C}_8\text{H}_{10}\text{O}_6\text{Cl}_2$  requires  $\text{Cl} = 26.01$  per cent.

The following polarimetric observations were made.



*Rotation of Methylic Di-monochloroacetyl-glycerate.*

Temp.	Observed rotation in 44 mm. tube.	Density compared with water at 4°.	$[\alpha]_D$	$[\delta]_D$
100°	- 10·49°	1·3251	- 17·99°	- 140·8
65	- 9·76	1·3662	- 16·24	- 129·7
40	- 9·04	1·3954	- 14·72	- 119·3
29·2	- 8·68	1·4099	- 13·99	- 114·1
15	- 8·10	1·4263	- 12·91	- 106·1

The density determinations actually made were

$$d\ 17^\circ/4^\circ = 1\cdot4240. \quad d\ 40^\circ/4^\circ = 1\cdot3954. \quad d\ 60^\circ/4^\circ = 1\cdot3722.$$

$$d\ 80^\circ/4^\circ = 1\cdot3480. \quad d\ 100^\circ/4^\circ = 1\cdot3251.$$

This substance subsequently crystallised spontaneously, and the solid melted at 43–44°.

*Ethylic Di-monochloroacetyltartrate.*—A mixture of 15 grams of ethylic tartrate ( $a_D = +8\cdot77^\circ$ ,  $t = 16^\circ$ ,  $l = 1$ ) and 80 grams of monochloroacetyl chloride was heated at 110° for three days, and then fractionated as before until the rotation was constant. The boiling point of the final product was 217° (oil bath 245°, pressure about 15 mm.).

The chlorine was determined by the Carius-Volhardt method.

- 0·2073 required 0·2011 AgNO<sub>3</sub>. Cl = 20·25 per cent.
  - 0·5428 gave 0·4418 AgCl (gravim.). Cl = 20·13 per cent.
- C<sub>12</sub>H<sub>16</sub>O<sub>8</sub>Cl<sub>2</sub> requires Cl = 19·78 per cent.

The following polarimetric observations were made.

*Rotation of Ethylic Di-monochloroacetyltartrate.*

Temp.	Observed rotation in 44 mm. tube.	Density compared with water at 4°.	$[\alpha]_D$	$[\delta]$
100°	+ 6·44°	1·2394	+ 11·81°	+ 96·84°
74·5	+ 5·89	1·2667	+ 10·57	+ 87·93
49·5	+ 5·29	1·2935	+ 9·29	+ 78·42
41	+ 5·11	1·3026	+ 8·92	+ 75·58
15·5	+ 4·33	1·3306	+ 7·40	+ 63·59

The following were the density determinations actually made.

$$d\ 18^\circ/4^\circ = 1\cdot3279. \quad d\ 40^\circ/4^\circ = 1\cdot3040. \quad d\ 60^\circ/4^\circ = 1\cdot2823.$$

$$d\ 80^\circ/4^\circ = 1\cdot2603. \quad d\ 100^\circ/4^\circ = 1\cdot2394.$$

After the above results had been obtained, we became aware of the fact that methylic, ethylic, propylic, and isobutylic di-monochloroacetyltartrates had already been prepared by Freundler (*Bull. soc. chim.*, 1895, [iii], 13, 1055–1063). The following figures are given by him for the ethylic compound.

B. p. 195–197° (12 mm. pressure), density at 15° = 1·311  $[\alpha]_D^{15^\circ} = +9\cdot4^\circ$ .

The specific rotation is thus higher by  $2^\circ$  than that found by us for the same temperature, whilst the density and boiling point are slightly lower.

In consequence of this discrepancy, the preparation of this compound has been repeated by one of us in conjunction with Dr. Turnbull, the results being recorded in the paper which follows this.

*Methylic Di-monochloroacetyltartrate*.—From 20 grams of methylic tartrate ( $\alpha_D = +4.57^\circ$ ,  $t = 16^\circ$ ,  $l = 2$ ) and 130 grams of monochloroacetyl chloride heated at  $110^\circ$  for 2 days, 30 grams of product were obtained, distilling between  $220^\circ$  and  $235^\circ$  (oil bath  $260^\circ$ , pressure about 15 mm.). This solidified when triturated with a solution of sodium carbonate, and, after drying on porcelain, was crystallised from toluene, the crystals washed with light petroleum and then distilled. The boiling point was  $217^\circ$  (oil bath  $260^\circ$ , pressure about 18 mm.), 15 grams of this purified product being obtained. The substance crystallises from toluene in large, truncated pyramids; the melting point was  $55^\circ$ .

The chlorine was determined by the Carius-Volhardt method.

1 0.2047 required 0.2092  $\text{AgNO}_3$ .  $\text{Cl} = 21.34$  per cent.

2. 0.2013        „        0.2059  $\text{AgNO}_3$ .  $\text{Cl} = 21.36$         „

$\text{C}_{10}\text{H}_{12}\text{O}_8\text{Cl}_2$  requires  $\text{Cl} = 21.45$  per cent.

The following polarimetric observations were made.

*Rotation of Methylic Di-monochloroacetyltartrate.*

Temp.	Observed rotation in 44 mm. tube.	Density compared with water at $4^\circ$ .	$[\alpha]_D$	$[\delta]_D$
$100^\circ$	$+1.50^\circ$	1.3264	$+2.57^\circ$	$+21.46^\circ$
75.3	$+0.76$	1.3547	$+1.27$	$+10.80$
54.7	$+0.25$	1.3784	$+0.41$	$+3.53$
43.2	$-0.05$	1.3915	$-0.08$	$-0.70$
33.6	$-0.16$	1.4026	$-0.26$	$-2.25$
14	$-0.50$	1.4250	$-0.80$	$-6.98$

The following were the density determinations actually made.

$d\ 19^\circ/4^\circ = 1.4193$ ,         $d\ 40^\circ/4^\circ = 1.3953$ ,         $d\ 60^\circ/4^\circ = 1.3722$ .

$d\ 80^\circ/4^\circ = 1.3492$ ,         $d\ 100^\circ/4^\circ = 1.3264$ .

Methylic di-monochloroacetyltartrate has also been prepared by Freundler (*loc. cit.*), who describes it as an extremely syrupy liquid distilling at about  $187$ — $190^\circ$  (14 mm. pressure) and of density 1.409 at  $18^\circ$ . The rotatory power he gives as

$$[\alpha]_D^{18} = +3.5^\circ \quad (l = 0.5, d = 1.409, \alpha_D = +2.26^\circ),$$

polarimetric results which are, therefore, even more at variance with ours than in the case of the corresponding ethylic compound referred

to above. His density is distinctly, and his boiling point considerably, lower than ours.

In consequence of this marked discrepancy, the preparation of this substance has also been repeated with some modifications by one of us in conjunction with Dr. Turnbull, and the results are recorded in the paper which follows this.

M. Freundler has determined also the molecular weights of the methylic and propylic salts of di-monochloroacetyltartaric acid by the cryoscopic method, using benzene and ethylenic dibromide as solvents, and we may take the opportunity of pointing out that he gives throughout an erroneous theoretical value for the molecular weight of each of these ethereal salts. Thus for the methylic di-monochloroacetyltartrate he makes all his calculations on the basis of the true molecular weight being 431 instead of 331, and in the case of the propylic compound he uses the molecular weight 487 instead of 387.

*Influence of the Chloroacetyl Groups on the Physical Properties.*

1. An examination of the results recorded in the preceding pages shows that the introduction of two monochloroacetyl groups

(a) Increases the lævo-rotation of methylic and ethylic glycerate, the effect being very similar to, but slightly greater than, that produced by the introduction of two acetyl groups, thus

Methylic glycerate .....	$[\alpha]_D^{15^\circ} = -4.80^\circ$
„ diacetylglycerate .....	$[\alpha]_D^{15^\circ} = -12.04$
„ dimonochloroacetylglycerate .....	$[\alpha]_D^{15^\circ} = -12.91$
Ethylic glycerate.....	$[\alpha]_D^{15^\circ} = -9.18$
„ diacetylglycerate .....	$[\alpha]_D^{15^\circ} = -16.31$
„ dimonochloroacetylglycerate .....	$[\alpha]_D^{15^\circ} = -16.80$

(b) Considerably reduces the dextro-rotation of methylic tartrate, and barely increases that of ethylic tartrate; the effect on the latter is, in fact, hardly appreciable. In this respect, the effect of the two monochloroacetyl groups resembles, although it is far inferior to, that produced by the introduction of two acetyl groups. Thus two acetyl groups greatly reduce the dextro-rotation of methylic tartrate, and very considerably reduce that of ethylic tartrate,

Methylic tartrate .....	$[\alpha]_D^{20^\circ} = +2.14^\circ$ (liquid).
„ diacetyltartrate .....	$[\alpha]_D^{25^\circ} = -15.1$ (in absolute alcoholic solution)
„ di-monochloroacetyltartrate...	$[\alpha]_D^{20^\circ} = -0.64$ (liquid).
Ethylic tartrate .....	$[\alpha]_D^{20^\circ} = +7.66^\circ$
„ diacetyltartrate.....	$l = 25^\circ, l = 1, \alpha = +5^\circ$
„ di-monochloroacetyltartrate...	$[\alpha]_D^{20^\circ} = +7.67^\circ$

All three ethylic salts were examined in the liquid state.

In this respect, our results are in direct opposition to those of M. Freundler, who finds that the introduction of the two monochloracetyl groups slightly but appreciably increases the dextro-rotation of both methylic and ethylic tartrates respectively. We would remark in this connection that we have obtained both the methylic and ethylic di-monochloracetyl tartrates in a crystalline state,\* whilst M. Freundler has only handled them in the liquid condition.

The diminution in the dextro-rotation of methylic and ethylic tartrate effected by the introduction of the two monochloracetyl groups is much more conspicuous if the rotations at a high temperature are taken into consideration, thus

Methylic tartrate .....	$[\alpha]_D^{100^\circ} = + 5.99^\circ$
,, di-monochloracetyltartrate .....	$[\alpha]_D^{100^\circ} = + 2.57^\circ$
Ethylic tartrate .....	$[\alpha]_D^{100^\circ} = + 13.29$
,, di-monochloracetyltartrate .....	$[\alpha]_D^{100^\circ} = + 11.81$

2. Similarly, the above results show that the introduction of two dichloracetyl groups

(a) Increases the lævo-rotation of both methylic and ethylic glycerate, the lævo-rotation of these di-dichloracetylglycerates being, however, only slightly greater than the corresponding di-monochloracetylglycerates; indeed, this relationship only holds good at low temperatures, for at high temperatures the lævo-rotation of the di-monochloracetylglycerates slightly but distinctly exceeds that of the corresponding di-dichloracetylglycerates. Thus—

	$[\alpha]_D^{15^\circ}$	$[\alpha]_D^{100^\circ}$	
Methylic glycerate .....	-4.80°	-8.31°†	(calculated).
,, diacetylglycerate .....	-12.04	-19.24†	(calculated).
,, di-monochloracetylglycerate..	-12.91	-17.99	
,, di-dichloracetylglycerate.....	-13.96	-17.18	
Ethylic glycerate .....	-9.18	-12.55†	(calculated).
,, diacetylglycerate.....	-16.31	-23.09†	(calculated).
,, di-monochloracetylglycerate...	-16.80	-22.08	
,, di-dichloracetylglycerate .....	-18.20	-21.1	

\* See the next paper.

† It should be pointed out that these values of  $[\alpha]_D$  at  $100^\circ$  have been calculated for methylic and ethylic glycerates and diacetylglycerates from the materials given in the papers by P. Frankland and MacGregor (Trans., 1893, **63**, 1415; Trans., 1894, **65**, 754; Trans., 1894, **65**, 768). These materials enable the observed rotation,  $\alpha_D$ , to be extrapolated for  $100^\circ$ , whilst the density for  $100^\circ$  has been calculated by means of the average decrement in density, 0.0012211, for  $1^\circ$  rise in temperature, this average decrement having been obtained from density observations made on ethylic mono-trichloracetyltartrate, methylic di-dichloracetyltartrate, ethylic di-dichloracetylglycerate, and methylic di-trichloracetylglycerate.

(b) Very greatly increases the dextro-rotation of both methylic and ethylic tartrate, thus:—

	$[\alpha]_D^{20}$
Methylic tartrate .....	+2.14°
„ di-dichloracetyltartrate	+11.9
Ethylic tartrate.....	+7.66
„ di-dichloracetyltartrate...	+16.3

The rotation of these di-dichloracetyltartrates is comparatively insensitive to temperature, the dextro-rotation of the ethylic compound increasing but slightly with rise of temperature, whilst that of the methylic compound very slightly declines under the same circumstances. But even if the rotations at 100° be compared, the introduction of the two dichloracetyl groups effects a large increase in the dextro-rotation of both methylic and ethylic tartrate. Thus

	$[\alpha]_D^{100}$
Methylic tartrate .....	+5.99°
„ di-dichloracetyltartrate	+10.9
Ethylic tartrate.....	+13.29
„ di-dichloracetyltartrate ...	+17.08

The effect on the dextro-rotation of methylic and ethylic tartrate produced by the introduction of the two dichloracetyl groups resembles that produced by the introduction of two phenacetyl groups. Thus

Methylic di-phenacetyltartrate.....	$[\alpha]_D^{18} = +14.5^\circ$ (Freundler).
Ethylic „ .....	$[\alpha]_D^{19} = +15.3$ „

3. The introduction of two trichloracetyl groups was only found possible in the case of the glycerates, both methylic and ethylic tartrates yielding only monacidyl derivatives.

The introduction of the two trichloracetyl groups has the effect of

(a) increasing the lævo-rotation of the methylic glycerate to a greater extent than the introduction of two dichloracetyl groups. This is, however, only the case at low temperatures, for the rotation of methylic di-trichloracetylglycerate, being but very slightly increased by rise of temperature, the lævo-rotation of methylic di-dichloracetylglycerate at 100° is markedly greater than that of methylic di-trichloracetylglycerate at this temperature. Thus at 100° the lævo-rotation of methylic glycerate is most increased by the introduction of the two monochloracetyl groups, and least by that of the two trichloracetyl groups.

The relative effects on the lævo-rotation of ethylic glycerate produced by the introduction of these several groups is exactly similar.

The rotation of ethylic di-trichloracetylglycerate is almost perfectly



insensitive to temperature, but, if anything, rise of temperature causes diminution in lævo-rotation.

	$[\alpha]_D^{15^\circ}$	$[\alpha]_D^{100^\circ}$	
Methylic glycerate .....	-4.80°	-8.31°*	(calculated).
„ diacetylglycerate .....	-12.04	-19.24*	(calculated).
„ di-monochloracetylglycerate	-12.91	-17.99	
„ di-dichloracetylglycerate...	-13.96	-17.18	
„ di-trichloracetylglycerate	-14.2	-15.3	
Ethylic glycerate .....	-9.18	-12.55*	(calculated).
„ diacetylglycerate .....	-16.31	-23.09*	(calculated).
„ di-monochloracetylglycerate	-16.80	-22.08	
„ di-dichloracetylglycerate ...	-18.20	-21.1	
„ di-trichloracetylglycerate ..	-18.7	-18.4	

It is interesting to compare with the above the rotation of the diphenacetylglycerates, of which only the methylic compound has been prepared by one of us (Trans., 1896, 69, 111).

Methylic diphenacetylglycerate	$[\alpha]_D^{15^\circ} = -16.0^\circ$
„ „	$[\alpha]_D^{100^\circ} = -13.4$

From these figures it will be seen that, in rotatory effect, the phenacetyl group differs even slightly more from the acetyl group than does the trichloracetyl group.

4. The introduction of a single trichloracetyl group into methylic and ethylic tartrate respectively produces a change in their rotation very similar to that which is effected by the introduction of two dichloracetyl groups into these same compounds, thus

	$[\alpha]_D^{20^\circ}$	$[\alpha]_D^{100^\circ}$
Methylic tartrate .....	+2.14°	+5.99°
„ di-dichloracetyltartrate .....	+11.9	+10.9
„ mono-trichloracetyltartrate.....	+8.4	+10.15
Ethylic tartrate.....	+7.66	+13.29
„ di-dichloracetyltartrate.....	+16.3	+17.08
„ mono-trichloracetyltartrate .....	+15.5	+17.6

In this connection, it is worthy of note that the introduction of a single monochloracetyl group† produces an effect closely resembling that which attends the introduction of the trichloracetyl group, thus

Ethylic mono-monochloracetyltartrate (slightly impure)	$[\alpha]_D^{20^\circ}$	$[\alpha]_D^{100^\circ}$
	+11.44°	+17.32°

and, as so frequently pointed out above, any preponderating influence of the di- and tri-chloracetyl groups as compared with that of the monochloracetyl group tends to become equalised at a high temperature.

5. The influence which the several groups under consideration in this paper exercise on the molecular deviation ( $[\delta]_D$ ) may be summarised in the following tabular statements.

\* The footnote on p. 195 applies also here.

† See p. 204, in next paper.

	$[\delta]_D^{15^\circ}$	Differences	
Methylic glycerate .....	-27.9°	$\left. \begin{array}{l} 52.1 \\ 26 \\ 23 \\ 16 \end{array} \right\} 78.1 \left. \begin{array}{l} \\ \\ \\ \end{array} \right\} 101.1 \left. \begin{array}{l} \\ \\ \\ \end{array} \right\} 117.1$	
„ diacetyl-glycerate .....	-80.0		
„ di-monochloracetyl-glycerate...	-106		
„ di-dichloracetyl-glycerate .....	-129		
„ di-trichloracetyl-glycerate .....	-145		
Ethylic glycerate .....	-52.8°	$\left. \begin{array}{l} 55.4 \\ 28.8 \\ 29 \\ 21 \end{array} \right\} 84.2 \left. \begin{array}{l} \\ \\ \\ \end{array} \right\} 113.2 \left. \begin{array}{l} \\ \\ \\ \end{array} \right\} 134.2$	
„ diacetyl-glycerate .....	-108.2		
„ di-monochloracetyl-glycerate ...	-137		
„ di-dichloracetyl-glycerate .....	-166		
„ di-trichloracetyl-glycerate .....	-187		
	$[\delta]_D^{15^\circ}$	Differences	
Methylic tartrate .....	+13°	$\left. \begin{array}{l} - \\ - \\ +123 \\ -43 \end{array} \right\} +20 \left. \begin{array}{l} \\ \\ \\ \end{array} \right\} +103 \left. \begin{array}{l} \\ \\ \\ \end{array} \right\} +60$	
„ diacetyl-tartrate .....	unknown		
„ di-monochloracetyl-tartrate ...	-7		
„ di-dichloracetyl-tartrate .....	+116		
„ mono-trichloracetyl-tartrate ...	+73		
Ethylic tartrate .....	+49°	$\left. \begin{array}{l} - \\ - \\ +92 \\ -20 \end{array} \right\} +14 \left. \begin{array}{l} \\ \\ \\ \end{array} \right\} +106 \left. \begin{array}{l} \\ \\ \\ \end{array} \right\} +86$	
„ diacetyl-tartrate .....	unknown		
„ di-monochloracetyl-tartrate .....	+63		
„ di-dichloracetyl-tartrate.....	+155		
„ mono-trichloracetyl-tartrate.....	+135		

The relationship between the rotations of the several compounds we have investigated, and the influence of temperature on the rotation of each, is best shown by means of the diagrams, pp. 199, 201.

From the diagram p. 201, it will be seen

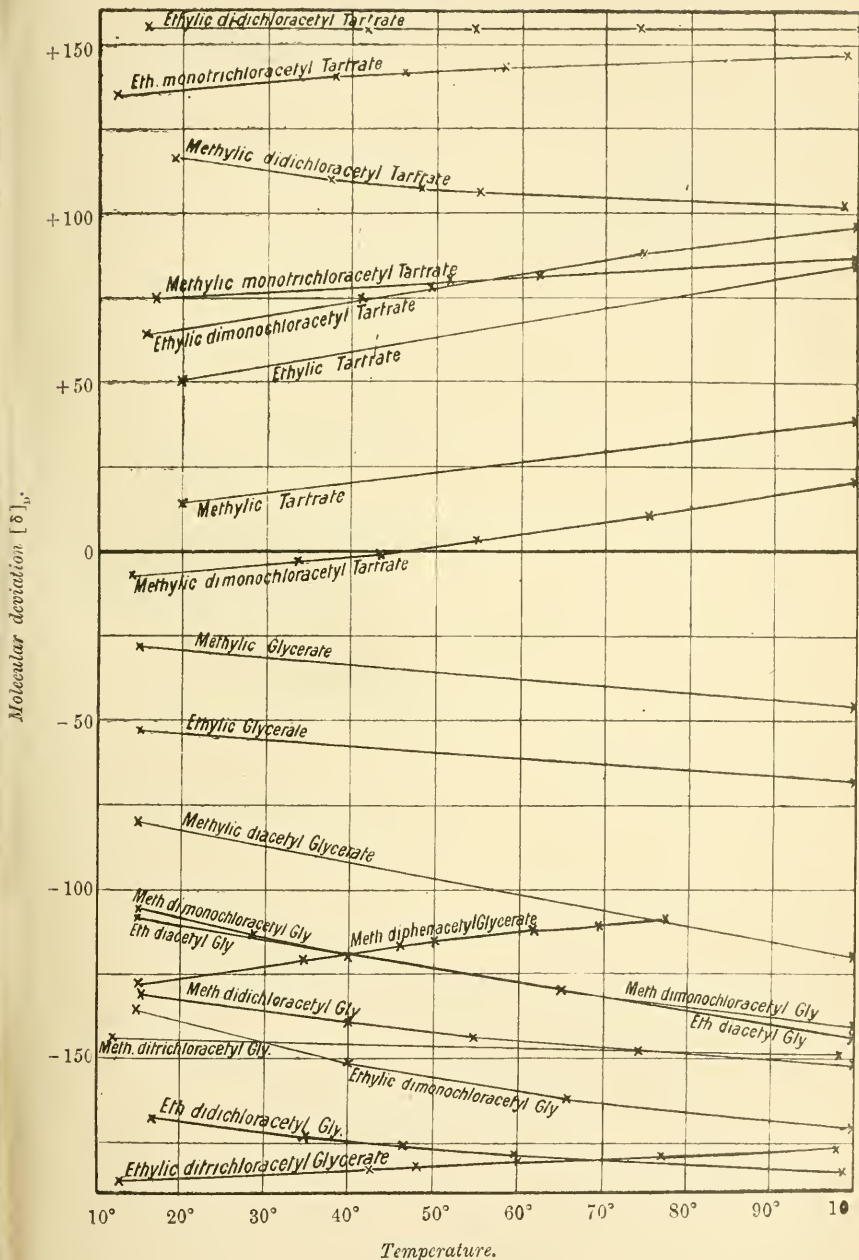
(a) That the specific rotations of methylic di-monochloracetyl-glycerate and methylic di-dichloracetyl-glycerate are identical at 62°, the rotations of the corresponding ethylic compounds becoming identical at 53°.

(b) That the methylic di-dichloracetyl-glycerate and di-trichloracetyl-glycerate have an identical specific rotation at 21°, the corresponding ethylic salts having also an identical specific rotation at 22°.

(c) That the specific rotations of the methylic di-trichloracetyl-glycerate and di-monochloracetyl-glycerate become equal at 37°, the rotations of the corresponding ethylic compounds, becoming equal at almost exactly the same temperature, namely, at 35°.

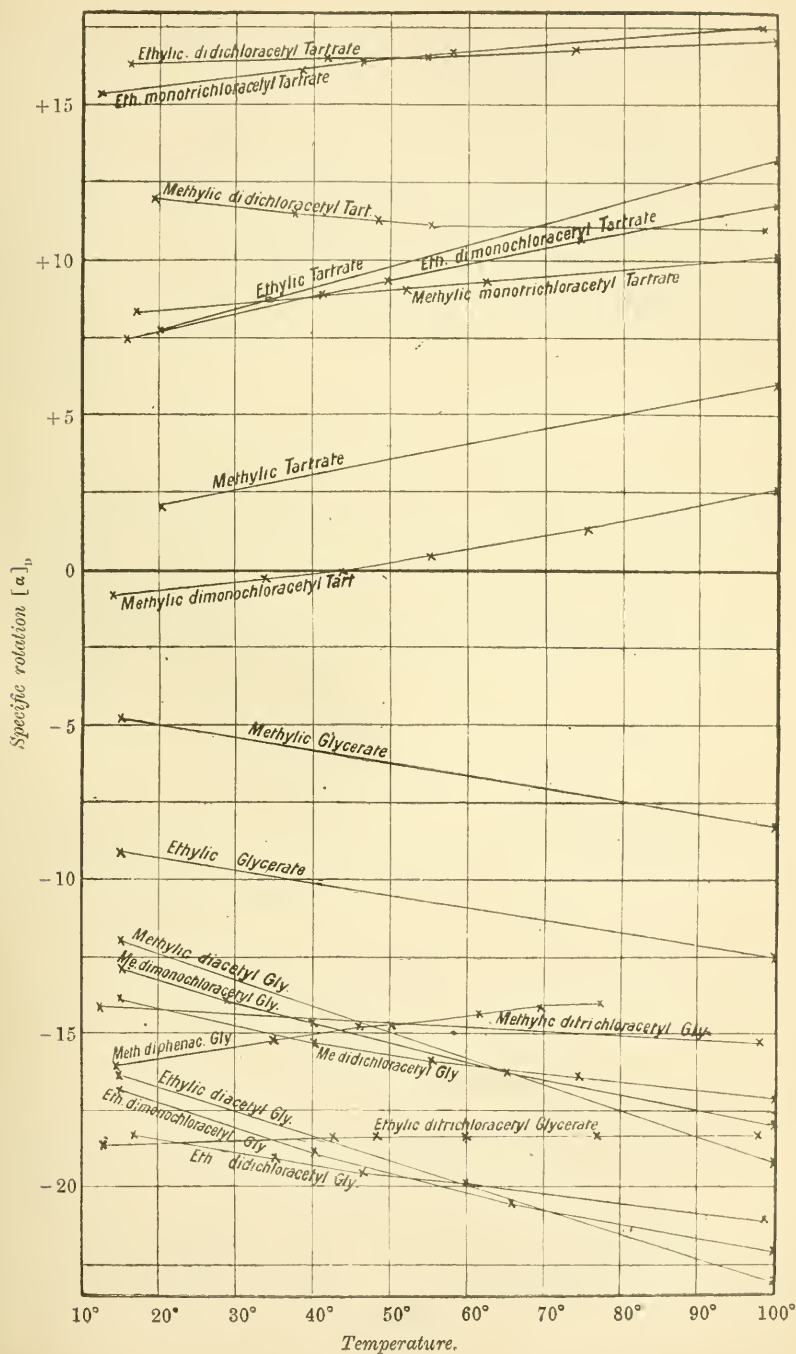
Thus it would appear that the influences which lead to an equal degree of asymmetry, in the case of the two methylic salts, are conditioned by the same, or nearly the same, temperature as conditions an equal degree of asymmetry in the case of the two ethylic compounds.

*Influence of Temperature on the Molecular Deviation of the Compounds described.*





*Influence of Temperature on the Specific Rotation of the Compounds described.*







# XIV.—*Rotation of Ethylic and Methylic Di-monochloracetyltartrates.*

By PERCY FRANKLAND, F.R.S., and ANDREW TURNBULL, Ph.D.

As pointed out in the previous paper (P. Frankland and Patterson, pp. 192, 193), the rotations, densities, and boiling points found for ethylic and methylic di-monochloracetyltartrates differ materially from those given for the same substances by Freundler (*Bull. soc. chim.*, 1895, [iii], 13, 1055—1063), and in order to put the accuracy of these results to the test we have again prepared these substances, using some modifications in the method, and redetermined their optical properties.

## *Ethylic Di-monochloracetyltartrate.*

*New Preparation, No. 1.*—In this case, 25 grams of ethylic tartrate ( $\alpha_D = +9.3^\circ$ , for  $20^\circ$  and  $l=1$ , or  $[\alpha]_D^{20} = +7.71^\circ$ ) were slowly added to 50 grams of monochloracetyl chloride (nearly double the theoretical quantity) heated in an oil bath at  $145^\circ$ , the temperature of the bath being then raised to  $160^\circ$  for 3 hours; the excess of acid chloride was then distilled off at the ordinary pressure, and the residue fractionated under diminished pressure. In this manner a product was obtained exhibiting the constant rotation

$$\alpha_D = +5.2^\circ, l = 0.498, t = 20^\circ; d_{20^\circ/4^\circ} = 1.3213.$$

$$[\alpha]_D^{20} = \frac{5.2}{0.498 \times 1.3213} = +7.90^\circ.$$

Thus both in the matter of density and rotation this product confirmed the results recorded in the preceding paper. The boiling point was  $207\text{--}208^\circ$  (12 mm. pressure).

The chlorine was also determined with the following results.

- |     |  |                            |                      |
|-----|--|----------------------------|----------------------|
| I.  | 0.2367 required  | 0.2232 AgNO <sub>3</sub> . | Cl = 19.69 per cent. |
|     | „ gave   | 0.1871 AgCl.               | Cl = 19.55 „         |
| II. | 0.2247 required  | 0.2109 AgNO <sub>3</sub> . | Cl = 19.60 „         |
|     | „ gave   | 0.1794 AgCl.               | Cl = 19.74 „         |
|     | C <sub>12</sub> H <sub>16</sub> O <sub>8</sub> Cl <sub>2</sub> requires Cl = 19.78 per cent. |                            |                      |

In addition to this, there was, however, a considerable quantity (17.8 grams) of a lower boiling fraction ( $185\text{--}198^\circ$  under 10 mm. pressure) obtained, which exhibited a rotation.

$$[\alpha]_D^{20} = \frac{12.4}{1.0045 \times 1.2825} = +9.62^\circ \quad (\alpha_D = +12.4^\circ, l = 1.0045, t = 20^\circ, d_{20^\circ/4^\circ} = 1.2825).$$

The chlorine was determined with the following results.

0.1845 required 0.1328  $\text{AgNO}_3$ . Cl = 15.03 per cent.

„ gave 0.1101  $\text{AgCl}$ . Cl = 14.76 „

Ethylic di-monochloroacetyltartrate,  $\text{C}_{12}\text{H}_{16}\text{O}_8\text{Cl}_2$  requires Cl = 19.78 %

„ mono-monochloroacetyltartrate,  $\text{C}_{10}\text{H}_{15}\text{O}_7\text{Cl}$ , „ Cl = 12.57 „

From this it would appear that the fraction of lower boiling point contains the monacidyl compound, which, on this hypothesis, has a higher dextro-rotation than the diacidyl salt.

We have pursued this question of the probable rotation of ethylic mono-monochloroacetyltartrate farther. Thus, after the above product had stood for many months, we fractionated it under diminished pressure, and obtained 8 grams boiling principally below  $104^\circ$ , and 6 grams boiling between  $175^\circ$  and  $197^\circ$  (pressure = 15 mm.). The fraction of low boiling point proved to be almost inactive; the higher fraction exhibited a rotation  $\alpha_D = +11.90^\circ$  ( $t = 20^\circ$ ,  $l = 1$ ), whilst the chlorine was only 9.57 per cent., and thus too low for ethylic mono-monochloroacetyltartrate. It was then dissolved in benzene, shaken up with water for 4 hours, and, after separating, the benzene solution was dried with anhydrous sodium sulphate, the benzene being finally evaporated. The rotation of the residue thus obtained was  $\alpha_D = +14.70^\circ$  ( $t = 20^\circ$ ,  $l = 1$ ).

0.1757 required 0.1093  $\text{AgNO}_3$ . Cl = 12.99 per cent.

„ gave 0.0922  $\text{AgCl}$ . Cl = 12.97 „

On combustion,

0.1679 gave 0.2580  $\text{CO}_2$  and 0.0783  $\text{H}_2\text{O}$ . C = 41.90; H = 5.18.

	Theory for ethylic	
	Mono- $\text{C}_{10}\text{H}_{15}\text{O}_7\text{Cl}$	Di-monochloroacetyltartrate. $\text{C}_{12}\text{H}_{16}\text{O}_8\text{Cl}_2$
Chlorine .....	12.57	19.78 per cent.
Hydrogen.....	5.31	4.46 „
Carbon .....	42.48	40.12 „

The above figures show that the product was ethylic mono-monochloroacetyltartrate, still mixed with a very small proportion of ethylic di-monochloroacetyltartrate. As we had not sufficient material for further purification, the specific rotation was determined at  $20^\circ$  and at  $100^\circ$ .

*Rotation of Ethylic Mono-monochloroacetyltartrate (slightly impure).*

Temp.	Observed rotation in 43.67 mm. tube.	Density compared with water at $4^\circ$ .	$[\alpha]_D$ .
$20^\circ$	+ 6.38	1.2775	+ 11.44°
$99.3$	+ 9.03	1.1937	+ 17.32

The density determinations actually made were,  $d_{20^{\circ}/4^{\circ}} = 1.2775$   
 $d_{62^{\circ}/4^{\circ}} = 1.2331$ .

Thus the above monacidyltartrate has a much higher detro-rotation than the corresponding diacidyl compound, the difference between the two increasing with rise of temperature.

*New Preparation, No. 2.*—Yet another preparation was made, again modifying the method. On this occasion, 27 grams of ethylic tartrate ( $[\alpha]_D^{20} = +7.71^{\circ}$ ) were slowly added to 120 grams of monochloracetyl chloride in an oil bath heated to  $142^{\circ}$ . The addition of the tartrate occupied 2½ hours, after which the temperature of the oil bath was raised, and maintained at  $160^{\circ}$  for 5 hours. The excess of acid chloride was distilled off, and the residue then fractionated under diminished pressure with the result that only about 1 c.c. passed over below  $185^{\circ}$  (14 mm. pressure), whilst 35 grams were obtained between  $190$ — $205^{\circ}$ . The latter fraction was dissolved in about 100 c.c. of benzene, and the solution shaken with a strong solution of sodium carbonate for 5 hours; after separation, the greater part of the benzene was distilled off, and the residue precipitated with light petroleum, this precipitation from benzene solution by means of light petroleum being repeated a second time. It was then found that the rotation was constant.

$$[\alpha]_D^{20} = \frac{10.22}{1.0 + 1.3213} = +7.74^{\circ}. \quad (a_D = +10.22^{\circ}, l = 1.0, t = 20^{\circ}, \\ d_{20^{\circ}/4^{\circ}} = 1.3213, \text{ the density was assumed to be the same as before.})$$

The product was then fractionally distilled under reduced pressure; only about 1 c.c. passed over below  $206^{\circ}$  (15 mm. pressure), practically the whole being obtained at  $205$ — $209^{\circ}$  (12 mm. pressure).

The rotation of this product was determined, after which it was re-fractionated under reduced pressure, nearly the whole passing over between  $207$  and  $209^{\circ}$  (17 mm. pressure, oil bath  $246^{\circ}$ ); as the rotation was now practically constant, the following more detailed polarimetric observations were made.

*Rotation of Ethylic Di-monochloracetyltartrate.*

*(New preparation before crystallisation.)*

Temp.	Observed rotation in 99.9 mm. tube.	Density compared with water at $4^{\circ}$ .	$[\alpha]_D$
$20^{\circ}$	+10.26	1.3227	+7.76°
$13.5$	+9.69	1.3301	+7.29
100	+14.81	1.2342	+12.01
72	+13.36	1.2643	+10.58
40	+11.55	1.3000	+8.89

The density determinations actually made were

$$d\ 18^{\circ}/4^{\circ} = 1.3250. \quad d\ 40^{\circ}/4^{\circ} = 1.3000. \quad d\ 60^{\circ}/4^{\circ} = 1.2773. \\ d\ 80^{\circ}/4^{\circ} = 1.2557. \quad d\ 100^{\circ}/4^{\circ} = 1.2342.$$

Hitherto the ethylic di-monochloracetyltartrate had only been obtained as a viscid liquid, and it is so described by Freundler also, but on allowing the product on which the above observations had been made to stand for a few days in a cold place, it set to a solid mass consisting of long, radiating, colourless needles; this was spread on porous porcelain to remove the small quantity of still liquid matter, and the previous preparations were also easily made to solidify by sowing with crystals; it was, however, not found possible to recrystallise the substance from solvents, since it always separated as an oil, so that the only available method of further purification consisted in spreading on porcelain before solidification was complete. After submitting the substance to this treatment, the melting point was found to be  $27^{\circ}$ , whilst the polarimetric results were

*Rotation of Ethylic Di-monochloracetyltartrate.*

*(New preparation after crystallisation.)*

Temp.	Observed rotation in 49.85 mm. tube.	Density compared with water at $4^{\circ}$ .	$[\alpha]_D$
$20^{\circ}$	+5.03°	1.3266	+7.61°
11.5	+4.66	1.3368	+6.99
100	+7.23	1.2340	+11.75
74	+6.58	1.2636	+10.45
40.5	+5.64	1.3013	+8.69

The density determinations actually made were

$$d\ 20^{\circ}/4^{\circ} = 1.3266. \quad d\ 40^{\circ}/4^{\circ} = 1.3019. \quad d\ 60^{\circ}/4^{\circ} = 1.2797. \\ d\ 80^{\circ}/4^{\circ} = 1.2570. \quad d\ 100^{\circ}/4^{\circ} = 1.2340.$$

With this solid product also, the following analytical determinations were made.

- I. 0.2003 required 0.1909  $\text{AgNO}_3$ .  $\text{Cl} = 19.90$  per cent.  
 „ gave 0.1628  $\text{AgCl}$ .  $\text{Cl} = 20.10$  „  
 II. 0.1954 required 0.1890  $\text{AgNO}_3$ .  $\text{Cl} = 20.20$  „  
 „ gave 0.1591  $\text{AgCl}$ .  $\text{Cl} = 20.13$  „  
 III. 0.1970 gave 0.2895  $\text{CO}_2$  and 0.0795  $\text{H}_2\text{O}$ .  $\text{C} = 40.07$ ;  $\text{H} = 4.48$ .  
 $\text{C}_{12}\text{H}_{16}\text{O}_8\text{Cl}_2$  requires  $\text{Cl} = 19.78$ ;  $\text{H} = 4.46$ ;  $\text{C} = 40.12$  per cent.  
 (Ethylic di-monochloracetyltartrate)

Thus the polarimetric results obtained with the crystalline substance differ but very slightly from those which we had previously observed



with the purified liquid products, and the difference, such as it is points to the dextro-rotation of the liquids being a very little too high probably in consequence of traces of the monacidyltartrate being still present; on this assumption, the still higher dextro-rotation of M. Freundler's liquid product is attributable to the presence of a larger proportion of monacidyltartrate, and that the latter possesses a much higher dextro-rotation we have shown on pp. 204—5.

*Methylic Di-monochloracetyltartrate.*

*New Preparation.*—Twenty-five grams of methylictartrate ( $\alpha_D = +2.79^\circ$ ,  $l = 1$ ,  $t = 20^\circ$ ) were slowly added to 96 grams of monochloracetyl chloride (b. p.  $103\text{--}105^\circ$ ) heated in an oil bath at  $145^\circ$ ; after the addition of the tartrate, which occupied about 2 hours, the temperature was maintained at  $145^\circ$  for 4 hours more. After the excess of acid chloride had been distilled off at atmospheric pressure, 54.5 grams being recovered, the residue was fractionated under reduced pressure, about 2 grams being obtained at  $96\text{--}110^\circ$  (15 mm. pressure), and the remainder at  $195\text{--}210^\circ$  (12 mm. pressure). The latter was refractionated, the main portion being collected between  $195^\circ$  and  $206.5^\circ$ . This was dissolved in benzene and shaken up with a solution of sodium carbonate for 4 hours; after separating, the benzene solution was dried with potassium carbonate and nearly all the benzene distilled off; on being kept for a few days in a cool place, white crystals separated, which were dried on porcelain and then crystallised from a mixture of benzene and light petroleum. The crystals thus obtained melted at  $54^\circ$ , but not sharply; on recrystallisation, a sharp melting point of  $55^\circ$ , as before, was obtained. The substance was again recrystallised and then analysed.

I. 0.1527 required 0.1599  $\text{AgNO}_3$ . Cl = 21.87 per cent.

„ gave 0.1335  $\text{AgCl}$ . Cl = 21.62 „

II. 0.2124 required 0.2206  $\text{AgNO}_3$ . Cl = 21.69 „

„ gave 0.1865  $\text{AgCl}$ . Cl = 21.71 „

III. 0.2328 gave 0.3120  $\text{CO}_2$  and 0.0787  $\text{H}_2\text{O}$ . C = 36.55; H = 3.76.

$\text{C}_{10}\text{H}_{12}\text{O}_8\text{Cl}_2$  requires Cl = 21.45; H = 3.63; C = 36.25 per cent.

(Methylic di-monochloracetyltartrate.)

The rotation having been shown to be unaffected by further recrystallisation, the following more detailed polarimetric observations were made.

*Rotation of Methylic Di-monochloracetyltartrate.**(New preparation.)*

Temp.	Observed rotation in 50·38 mm. tube.	Density compared with water at 4°.	$[\alpha]_D$
100°	+1·62°	1·3245	+2·43°
72—72·5	+0·73	1·3575	+1·07
59	+0·35	1·3735	+0·51
41—41·5	-0·01	1·3945	-0·01
24—24·5	-0·47	1·4171	-0·66
18	-0·49	1·4251	-0·68

The following were the density determinations actually made

$$d\ 20^\circ/4^\circ = 1\cdot4224. \quad d\ 40^\circ/4^\circ = 1\cdot3957. \quad d\ 60^\circ/4^\circ = 1\cdot3723.$$

$$d\ 80^\circ/4^\circ = 1\cdot3476. \quad d\ 100^\circ/4^\circ = 1\cdot3245.$$

This re-preparation of the methylic salt has, as in the case of the ethylic compound, therefore, only served to confirm the results recorded in the preceding paper.

The repeated preparation of the ethylic and methylic di-monochlor-acetyltartrates by two different operators, as recorded in this and the foregoing paper, in each case with practically the same result, and the fact that both compounds have ultimately been obtained by us in the crystalline form, would appear to place the figures which we have given for the rotation, density, &c., of these substances altogether beyond question.

The principal difficulty attending the preparation of these compounds is the circumstance that, unless a large excess of the acid chloride be employed, a considerable proportion of the monacidyltartrates will be formed, and these, as we have shown, possess a markedly greater dextro-rotation, so that unless these monacidyltartrates are carefully removed, the rotation obtained for the di-acidyl compound, will be too high.

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# XV.—*A Chemical Investigation of the Constituents of Indian and American Podophyllum (Podophyllum emodi and Podophyllum peltatum).*

By WYNDHAM R. DUNSTAN, F.R.S., and T. A. HENRY, Salters' Research Fellow in the Laboratories of the Imperial Institute.

*Podophyllum emodi* is a small, herbaceous plant which grows abundantly in Northern India; it is figured and briefly described in Royle's *Illustrated Botany of the Himalayas*. The root, or, more strictly, the rhizome, has long been used in Indian medicinal practice for the same purpose as that for which the allied American plant, *Podophyllum peltatum*, is employed in Europe and America. It acts as a powerful purgative, and, in particular, beneficially affects the liver. It has been frequently suggested that the constituents of both rhizomes are very similar, but they have never been completely examined (Watt's *Dictionary of the Economic Products of India*, 6, Part I.; Dymock, *Imperial Institute Handbooks of Commercial Products*, No. 3; Umney, *Pharm. Journal*, [iii], 12, 217; Thompson, *Amer. Journ. Pharm.*, 1891).

The chemical constituents of the rhizome of the American *Podophyllum peltatum* have, however, been made the subject of several investigations. First, in 1832, Hodgson prepared the mixture of resins known and largely used in medicine as "podophyllin," by precipitating a concentrated alcoholic extract of the rhizome with water; this is now manufactured on a large scale, and is the form in which 'podophyllum' is usually administered as a drug. The first important contribution to the chemistry of podophyllum was that made by Podwyssotski (*Pharm. Journ.*, [iii], 12, 217, 1011); this chemist showed that the rhizome did not, as was previously supposed, contain the alkaloid berberine; he isolated from it three substances which he named *podophyllotoxin*, *podophyllic acid*, and *podophylloquercetin* respectively. To the first of these he attributed the characteristic purgative action of the drug, but the others he believed to be physiologically inert; the first two he did not succeed in obtaining in a crystalline condition, the third was a crystalline, yellow colouring matter.

He further showed that when podophyllotoxin is acted on by alkaline solutions, it is decomposed, furnishing two new substances, one crystallising in long needles with a silky lustre, which he named *picropodophyllin*, and the other a gelatinous substance having the characters of an acid, which he called *picropodophyllic acid*.

Kursten (*Arch. Pharm.*, 1891, 229, 220—248), who considerably

amplified the work of Podwyssotski, succeeded in crystallising podophyllotoxin, and ascribed to it the composition represented by the formula  $C_{23}H_{24}O_9, 2H_2O$ . He showed also that by the action of alkalis it is converted into an isomeride picropodophyllin, and concluded that the picropodophyllic acid of Podwyssotski simultaneously produced is an oxidation product which can be prepared by the action of permanganate in alkaline solution. He expressed its composition by the formula  $C_{20}H_{24}O_9$  and called it podophyllic acid. He obtained this acid crystalline, and ascertained its molecular weight through the analysis of its copper salt; he also determined that both picropodophyllin and podophyllotoxin have the same composition, and contain three methoxyl groups. The composition of Podwyssotski's podophylloquercetin he represented by the formula  $C_{23}H_{16}O_{10}$ , and prepared crystalline hexacetyl and hexabenzoyl derivatives from it; from an examination of these derivatives, and of the methyl ether of the colouring matter, he came to the conclusion that podophylloquercetin and quercetin (from quercitron bark) are not identical.

Very little has so far been done in the chemistry of *Podophyllum emodi*. The amount of resin in the rhizome has been estimated by Dymock and Hooper (*Pharmacographia Indica*), and also by J. C. Umney (*Pharm. Journ.*, [iii], 23, 207), who showed that it contains Podwyssotski's amorphous podophyllotoxin, but in smaller quantity than the American rhizome.

The objects of the present investigation were to decide whether or not the constituents of the American and Indian plants are identical, to determine their constitutions as far as possible, and to ascertain whether the rhizome of the latter plant could be used as a source of the medicinal resin 'podophyllin.' In addition to the chemical examination, physiological and therapeutical investigations of the action of the several constituents have been instituted, and the results of these will be separately published.

Briefly stated, the principal results we have obtained are as follows. We have proved that the constituents of *P. emodi* are identical with those of *P. peltatum*. Crystalline podophyllotoxin is shown to have the composition represented by the formula  $C_{15}H_{14}O_6, 2H_2O$ ; when acted on by aqueous alkalis it is converted into the isomeric picropodophyllin; the gelatinous acid first produced in this reaction is the acid corresponding to the lactone picropodophyllin, and not an oxidation product, as Kursten supposed. It is also shown that both podophyllotoxin and picropodophyllin contain two methoxyl groups, that both furnish monobromo-derivatives, and, when fused with potash, yield orcinol and acetic acid, also that both furnish dimethylnaphthalene when distilled with zinc dust. The formula  $C_{15}H_{14}O_6$  is assigned to podophyllotoxin and picropodophyllin, and  $C_{15}H_{16}O_7$  to

podophyllic acid, and structural formulæ are suggested for these substances, exhibiting them as derivatives of a substituted phenylated hydro- $\gamma$ -pyrone. The yellow colouring matter has been completely purified, analysed, and shown to have the composition represented by the formula  $C_{15}H_{10}O_7$ ; it yields a pentacetyl derivative melting at  $192^\circ$ , a tetramethyl ether (m. p.  $156^\circ$ ), and a compound with sulphuric acid corresponding exactly with the quercetin compound. When fused with potash, it yields phloroglucinol and protocathechuic acid. From this experimental evidence it is concluded that the colouring matter is identical with the quercetin of quercitron bark, and that, therefore, the use of the name podophylloquercetin is unnecessary.

The removal of podophyllotoxin and podophylloquercetin from 'podophyllin' left a dark coloured, resinous powder, which was still physiologically active; attempts were therefore made to isolate this active substance from the residue. By treating it with absolute alcohol, followed by fractional precipitation of the solution with water, a viscid, brown resin was obtained, which proved to be active as a purgative; all attempts to crystallise this viscid resin were unsuccessful. In the purest form in which we have obtained it, it is a transparent, reddish-brown substance, softening and becoming semi-liquid a few degrees above the atmospheric temperature. It yields a crystalline acetyl derivative, and from this we have ascertained indirectly that the podophyllo-resin probably has the formula  $C_{12}H_{12}O_4$ .

We are indebted to Dr. H. W. G. Mackenzie, assistant physician to St. Thomas's Hospital, and Mr. W. Dixon, M.B., Salters' Research Fellow in Pharmacology at St. Thomas's Hospital, for having examined the therapeutic effects and the physiological action of the constituents we have obtained from *Podophyllum emodi*. An account of their work will be published in a separate form, and only the general conclusions will be indicated here. Therapeutic trial has proved that the podophyllin prepared from *Podophyllum emodi* is as valuable a purgative as the podophyllin obtained from *P. peltatum*. The action of this resinous mixture is due partly to the podophyllotoxin it contains, and partly to the active 'podophyllo-resin' mentioned above. Owing to its intensely irritating action internally, even when given in small doses, podophyllotoxin is unsuitable as a medicinal substitute for podophyllin, whilst podophyllo-resin would seem to present no therapeutic advantage as compared with the podophyllin now employed. Picropodophyllin, picropodophyllic acid, and the quercetin are very slightly, if at all, active as purgatives.

Since *P. emodi* furnishes more podophyllin than *P. peltatum*, the Indian plant is of greater value as the source of this resin. Appended to this paper are results of determinations of the amount of resin contained in the rhizomes of plants collected in different districts of the



Punjab under the supervision of Dr. George Watt, C.I.E., Reporter on Economic Products to the Government of India.

*Podophyllotoxin.*

Podwyssotski had shown that podophyllotoxin is precipitated when a chloroform extract of the rhizome of *P. peltatum* is added to a large excess of light petroleum, and Kursten had found that by fractionally precipitating a chloroform solution of this crude podophyllotoxin a crystalline substance (podophyllotoxin) could be obtained. The method we finally adopted, after many trials, consisted in preparing the mixture of resins (podophyllin) from the rhizome of *P. emodi* and then percolating this, in a Soxhlet extractor, with chloroform; the chloroform was distilled from the percolate, the dark brown extract boiled with benzene, and the hot benzene solution filtered into a cold flask and allowed to cool somewhat; by this means, a good deal of resin was easily removed. The solution was then poured from the deposited resin, boiled for some time with animal charcoal, filtered, and set aside for several days, when almost colourless crystals of podophyllotoxin were obtained. These were purified by recrystallisation either from a mixture of chloroform and petroleum, or from alcohol and water.

The pure substance, which forms colourless needles melting at  $117^{\circ}$ , is easily soluble in alcohol, acetone, chloroform, and hot benzene, but only slightly in water. Its taste is very bitter. Analysis of a carefully purified specimen, which had been dried at  $110^{\circ}$  until no further loss of water occurred, gave the following results.

0.1121 gave 0.2534  $\text{CO}_2$  and 0.514  $\text{H}_2\text{O}$ . C = 61.65; H = 5.09.

0.142    ,,   0.3246  $\text{CO}_2$     ,,   0.611  $\text{H}_2\text{O}$ . C = 62.24; H = 4.78.

0.1328    ,,   0.3025  $\text{CO}_2$     ,,   0.0667  $\text{H}_2\text{O}$ . C = 62.13; H = 5.57.

Mean C = 62.00; H = 5.11.  $\text{C}_{15}\text{H}_{14}\text{O}_6$  requires C = 62.06; H = 4.82 p. c.

We therefore adopt this formula as simpler than that suggested by Kursten,  $\text{C}_{23}\text{H}_{24}\text{O}_9 \cdot 2\text{H}_2\text{O}$ .

*Specific Rotation of Podophyllotoxin.*—For the determination of this constant, an alcoholic solution containing 2.417 grams in 100 c.c. of absolute alcohol was used in a 2-decimetre tube with Laurent's half-shade polarimeter. The compound is strongly laevorotatory.

The mean of ten readings was  $-4^{\circ} 35'$ .

Hence the specific rotation  $[\alpha]_D$  is  $\frac{100 \times 4^{\circ} 35'}{2 \times 2.417} = -94^{\circ} 48'$ .

*Water of Crystallisation.*—When podophyllotoxin is crystallised from a mixture of alcohol and water, it separates as a hydrate. A determination of the water gave the following result.

0.2988 dried at  $100^{\circ}$  for 2 hours lost 0.0302; further dried at  $110^{\circ}$  until the weight was constant, it lost 0.0013; no further loss occurred at  $120^{\circ}$ . 0.2988 therefore contains  $0.0315 = 10.5$  per cent.  $C_{15}H_{14}O_6 \cdot 2H_2O$  requires 11.2 per cent. of water of crystallisation.

*Anhydrous Podophyllotoxin.*—The dried podophyllotoxin obtained in the previous experiment was dissolved in absolute alcohol, and the solvent then removed by exposure in a vacuum desiccator. As the solution became concentrated, crystals of anhydrous podophyllotoxin melting at  $157^{\circ}$  were obtained; these pass into the ordinary hydrated substance when recrystallised from alcohol by adding water. It was afterwards found that a very convenient method of obtaining anhydrous podophyllotoxin consists in heating the hydrated substance at its melting point ( $117^{\circ}$ ) for a few minutes, dissolving the product in dry chloroform, and adding dry light petroleum until the mixture is slightly turbid; after standing a few hours, the anhydrous substance crystallises out. On exposure to air and light for several weeks, anhydrous podophyllotoxin acquires a purple colour; the hydrated substance, on the contrary, appears to be quite stable under these conditions. The specific rotation of an alcoholic solution of anhydrous podophyllotoxin was found to be  $[\alpha]_D = -78^{\circ} 4'$ .

#### ↓ *Picropodophyllin.*

If podophyllotoxin is boiled with aqueous alkalis until completely dissolved, and the liquid is then acidified with dilute mineral acids, a white precipitate is thrown down; this is soluble in hot alcohol, and on cooling is deposited in the form of silky masses of long needles, melting at  $227^{\circ}$ . It has all the properties of Podwyssotski's picropodophyllin. It was found to be soluble in chloroform, acetone, and hot alcohol, and nearly insoluble in cold alcohol and water. Like podophyllotoxin, it has an extremely bitter taste, but has no rotatory action on polarised light. Analysis of a carefully purified specimen gave the following results.

0.0895 gave 0.203  $CO_2$  and 0.0436  $H_2O$ . C = 61.86; H = 5.42.  
 0.1253 „ 0.2841  $CO_2$  „ 0.0604  $H_2O$ . C = 61.74; H = 5.35.  
 Mean C = 61.8; H = 5.38.  $C_{15}H_{14}O_6$  requires C = 62.06; H = 4.82 per cent.

Picropodophyllin, therefore, appears to be isomeric with podophyllotoxin. As further proof of the isomerism of podophyllotoxin and picropodophyllin, it should be added that when podophyllotoxin is heated in sealed tubes with water or dilute hydrochloric acid, some picropodophyllin is formed, and although decomposition products, such as methylic alcohol, &c., have been carefully searched for, none have been found.

The difference of even a methyl group makes a considerable difference

in the percentage composition of this molecule ; thus, supposing picropodophyllin to be methylpodophyllotoxin,  $C_{15}H_{13}O_6 \cdot CH_3$ , this formula would require C = 63.15 ; H = 5.2 per cent.

The results of the combustion of picropodophyllin recorded above cannot be reconciled with this, and the presence of an extra methoxyl or acetyl group would make the difference greater still.

On the other hand, the combustions of podophyllotoxin are uniformly slightly lower in carbon than those of picropodophyllin.

Podophyllotoxin ...	61.64	61.53	61.13	61.51	61.40	mean 61.4
Picropodophyllin...	61.86	61.74	61.93			„ 61.8

But we believe that this is explained by the difficulty of obtaining podophyllotoxin completely anhydrous. The facts recorded subsequently greatly strengthen the supposition that the two compounds are isomeric.

From the experiments we have made, it does not appear that picropodophyllin is an actual constituent of the plant.

#### ✓ *Podophyllic Acid.*

If the solution obtained by boiling podophyllotoxin with alkali is carefully cooled and then acidified by adding dilute acetic acid, no precipitation occurs, but on standing for several hours (unless the solution is very concentrated) the whole solidifies to a transparent jelly. If this jelly is dissolved in alcohol and the solution allowed to stand, almost the whole of the podophyllotoxin originally used is obtained in the form of picropodophyllin. It is therefore evident that a very close connection exists between picropodophyllin and the gelatinous acid, which is probably the principal constituent of Podwysotski's picropodophyllic acid, and Kursten's podophyllic acid. We propose to retain for it the name of *podophyllic acid*.

If picropodophyllin itself is boiled with alkalis it dissolves, and if this solution is cooled and acidified with acetic acid, it also gelatinises.

All attempts to isolate this gelatinous substance failed ; when dissolved, it invariably gives only picropodophyllin on removing the solvent, and when exposed in the vacuum desiccator, it leaves only a mass of crystals of picropodophyllin. It is apparently an acid, since it redissolves on the addition of alkaline solutions, but as it does not react with any of the ordinary indicators, it is difficult to prepare salts by direct neutralisation. It was found possible, however, to prepare crystalline salts by the following method. Picropodophyllin or podophyllotoxin is dissolved in hot alcohol, and a sufficient quantity of alcoholic soda added to this solution, the mixture is then boiled for some time, and when crystals begin to form the mixture is allowed to cool, and the crystalline precipitate filtered off, washed once or twice

with alcohol and ether, and dried. It can be recrystallised from water or alcohol.

An aqueous solution of this substance gelatinises when acidified with acetic acid, and from this gelatinous material picropodophyllin is obtained by dissolving it in hot alcohol, and the substance when heated in a dry test tube yields a residue of sodium carbonate; the substance must therefore be the sodium salt of podophyllic acid.

From this crystalline sodium salt, a *silver* salt was prepared by double decomposition. Silver podophyllate is somewhat soluble in water, and is very unstable, becoming dark grey in a few minutes when exposed to light.

Analysis of two specimens gave the following results.

0.0745 gave 0.0195 Ag. Ag. = 26.17 }  
 0.0706 „ 0.0178 Ag. Ag. = 25.21 } Mean Ag = 25.69 per cent.

$C_{14}H_{15}O_5 \cdot COOAg$  requires Ag = 25.82 per cent.

The copper salt was prepared by adding solution of copper acetate to a solution of sodium podophyllate and slowly removing the water by evaporation in a desiccator; it is thus easily obtained in light green prisms. When boiled with alcohol or water, the copper salt decomposes, giving copper oxide, picropodophyllin crystallising from the alcoholic solution; this decomposition was made use of for the determination of the amount of copper contained in the salt.

0.1030 gave 0.0128 CuO = 12.42 per cent.

$(C_{15}H_{15}O_7)_2Cu$  requires Cu = 11.8 per cent.

The aqueous solution of sodium podophyllate is lævorotatory; a determination of the specific rotation, using a solution containing 2.7365 grams in 100 c.c. of solution in a 2-decimetre tube with Laurent's half-shade polarimeter, gave as the mean of ten readings  $4^\circ 33'$ .

Hence the specific rotation

$$[\alpha]_D = \frac{100 \times 4^\circ 33'}{2.7365 \times 2} = - 83^\circ 8'.$$

From the experimental facts mentioned, it is clear that picropodophyllin must be the anhydride of podophyllic acid. These facts may be summarised thus.

- (1) Picropodophyllin, when boiled with alkali, gives podophyllic acid.
- (2) Podophyllic acid loses water and becomes picropodophyllin.
- (3) The copper salt of podophyllic acid is decomposed on boiling with alcohol into cupric oxide and picropodophyllin, water being eliminated; picropodophyllin must therefore contain the group  $-CO \cdot O-$ .

It was thought that possibly the gelatinous acid produced from podophyllotoxin might be an optical isomeride of that obtained from

picropodophyllin, but the determination of the specific rotation of the former shows that the two are identical; this determination was carried out under the conditions mentioned above, using a solution containing 1.267 grams in 100 c.c.

The mean of ten readings was  $-2^{\circ} 7'$ .

Specific rotation  $[\alpha]_D = -83^{\circ} 31'$ .

From these observations, we conclude that Podwyssotski's picropodophyllin acid, is not, as Kursten supposes, an oxidation product of podophyllotoxin having the formula  $C_{20}H_{24}O_9$ , but when pure is a monobasic acid of the formula  $C_{15}H_{16}O_7$ , of which picropodophyllin ( $C_{15}H_{14}O_6$ ) is the anhydride or lactone.

*Determination of Methoxyl in Podophyllotoxin and Picropodophyllin.*

This estimation was carried out by Zeisel's method; two experiments gave the following results.

0.203 podophyllotoxin gave 0.3159 AgI.  $CH_3O = 20.61$ .

0.1226       "       "       0.1918 AgI.  $CH_3O = 20.71$ .

$C_{13}H_8O_4(OCH_3)_2$  requires  $CH_3O = 21.2$  per cent.

The determination of methoxyl groups in picropodophyllin gave the following results.

0.2068 picropodophyllin gave 0.3346 AgI.  $CH_3O = 21.43$ .

0.134       "       "       0.2204 AgI.  $CH_3O = 21.7$ .

$C_{13}H_8O_4(OCH_3)_2$  requires  $CH_3O = 21.2$  per cent.

Podophyllotoxin and picropodophyllin, therefore, both contain two methoxyl groups.

*Action of Fused Potash on Podophyllotoxin.*

Guareschi (*Ber.*, 1879, 12, 683) has examined the action of fused potash on "podophyllin," which he recognises to be a mixture, and found that paroxybenzoic acid, pyrocatechol and protocathechuic acids were the principal products.

When podophyllotoxin is added to melted potash and the mixture kept just fused for about half an hour, a dark brown "melt" is formed. This was dissolved in water, dilute sulphuric acid added in excess, the precipitate dissolved in ether, and after the ethereal solution had been decolorised with animal charcoal, the solvent was removed by distillation, and the residue dissolved in boiling water, and precipitated with a solution of basic lead acetate. This precipitate was decomposed with dilute sulphuric acid, the mixture shaken with ether, the ethereal solution dried over fused calcium chloride, and light petroleum added until



the mixture was just turbid. At first a resinous substance was deposited, but the later fractions consisted of a substance crystallising in colourless needles, and melting, after having been dried in the desiccator for some days, at  $107^{\circ}$ . It gave a violet coloration with ferric chloride solution. It had, therefore, the properties of *oreinol*, but the quantity obtained was insufficient for analysis.

The solution of the melt, which had been acidified with dilute sulphuric acid, was distilled, and the distillate, after being exactly neutralised with soda, was concentrated. Silver nitrate was then added and the white, crystalline precipitate collected, dried, and analysed.

0.0892 silver salt gave 0.0573 Ag.  $\text{Ag} = 64.2$ .

Silver acetate requires  $\text{Ag} = 64.61$  per cent. The volatile acid is therefore *acetic acid*.

No derivatives were obtained when podophyllotoxin or picropodophyllin was allowed to react with acetic anhydride, benzoic chloride, or hydroxylamine; in each case the substance was recovered unchanged.

When solutions of podophyllotoxin and phenylhydrazine interact, an oily precipitate forms on standing, but this could not be obtained in a crystalline condition, and has not been further examined.

#### *Action of Bromine on Podophyllotoxin.*

Finely powdered podophyllotoxin was made into a paste with glacial acetic acid, and bromine added until a slight excess was present; the acetic acid was then removed by exposure in a vacuum desiccator, the residue dissolved in ether, the solution decolorised with charcoal, and sufficient light petroleum added to cause slight turbidity on standing. In this way, colourless crystals of a bromo-derivative melting above  $250^{\circ}$  were obtained; this, after recrystallisation from ether and petroleum, was analysed by Carius' method.

0.116 gave 0.0568 AgBr.  $\text{Br} = 20.9$ .

$\text{C}_{15}\text{H}_{14}\text{O}_6\text{Br}$  requires  $\text{Br} = 21.6$  per cent.

#### *Action of Bromine on Picropodophyllin.*

A bromo-derivative of picropodophyllin was formed on treating it with bromine in the same manner as podophyllotoxin, but it could not be obtained in a crystalline condition except from alcohol, and solution in this liquid was always accompanied by liberation of free bromine. A specimen which had been crystallised from alcohol was dissolved in ether, and the solution fractionally precipitated with light petroleum; the second fraction was colourless and melted at  $138^{\circ}$ , and no change in the melting point was observed after fractional precipitation from

ether. A portion of this specimen was analysed, with the following result.

0.0347 gave 0.0143 AgBr. Br = 18.85

$C_{15}H_{14}O_6Br$  requires Br = 21.6 per cent.

This monobromopicropodophyllin, therefore, appears to be an isomeric form of monobromopodophyllotoxin.

*Action of Nitric Acid on Podophyllotoxin and on Picropodophyllin.*

On adding strong nitric acid to podophyllotoxin dissolved in glacial acetic acid, a deep red coloration was produced, which, after a few hours, changed to deep yellow; after the nitric and acetic acids had been partly removed by heating on a water bath, a colourless, crystalline substance separated, which was shown to be *oxalic acid* by an analysis of the silver salt.

Found Ag = 70.5.  $Ag_2C_2O_4$  requires Ag = 70.8 per cent.

It should be added here that the substance melted at  $100^\circ$  before drying, and at  $187^\circ$  after drying, which is characteristic of oxalic acid.

The residue left after complete removal of the nitric acid and acetic acid was an amorphous, yellow resin; from this, no crystalline substance could be isolated.

Picropodophyllin was found to yield exactly the same products as podophyllotoxin when attacked by nitric acid.

*Distillation of Podophyllotoxin with Zinc Dust.*

When podophyllotoxin is mixed with a large excess of zinc dust and the mixture heated to redness in a tube, a small quantity of a yellow oil is obtained; by using considerable quantities of podophyllotoxin, enough of this oil was finally accumulated for analysis. It was purified by dissolving in ether, and after shaking with dilute alkali, which removed some phenolic substance, the ether was distilled off, the last traces being removed by exposure in a vacuum, and the oily residue distilled. The portion boiling between  $256^\circ$  and  $258^\circ$  (about 80 per cent. of the product) was pale yellow, and had a slight phenolic odour; when exposed to the air for several days, it darkened and somewhat resinified; on adding picric acid to its ethereal solution, it became deep red and deposited orange-red crystals melting at  $134^\circ$  (dimethylnaphthalene picrate melts at  $136^\circ$ ).

The oil gave the following numbers on analysis.

0.1547 gave 0.5181  $CO_2$  and 0.1166  $H_2O$ . C = 91.3; H = 8.3.

Dimethylnaphthalene requires C = 92.2; H = 7.69 per cent.

Picropodophyllin also furnishes dimethylnaphthalene when distilled with zinc dust.

✓ *The Colouring Matter.*

The residue left after removal of the ether from the ethereal solution obtained from the resin previously extracted by chloroform was treated with a small quantity of ether to remove resinous substances. The residue was then dissolved in hot glacial acetic acid, from which, on cooling, it crystallised in needles; these were then recrystallised from ether and chloroform. Prepared in this way, the colouring matter has the appearance of ordinary quercetin, and agrees with it in properties and composition.

Analysis gave the following numbers.

0.1239 gave 0.2730  $\text{CO}_2$  and 0.042  $\text{H}_2\text{O}$ .  $\text{C} = 60.09$ ;  $\text{H} = 3.71$ .

0.1034 „ 0.2293  $\text{CO}_2$  „ 0.034  $\text{H}_2\text{O}$ .  $\text{C} = 60.44$ ;  $\text{H} = 3.46$ .

$\text{C}_{15}\text{H}_{10}\text{O}_7$  requires  $\text{C} = 59.6$ ;  $\text{H} = 3.31$  per cent.

A compound of the colouring matter with sulphuric acid was prepared according to the method described by A. G. Perkin (Trans., 1895, 67, 647), the addition of sulphuric acid to a saturated solution of the colouring matter in hot acetic acid; on cooling, this solution deposited rosettes of a brilliantly orange coloured compound. These crystals were dried on a porous tile, and after being exposed for some time in a vacuum desiccator to remove acetic acid, were decomposed with water, and the amount of sulphuric acid liberated determined by titration.

0.112 gave sulphuric acid requiring 2.9 c.c. N/5 soda for neutralisation.  $\text{S} = 8.196$  per cent.

0.075 gave sulphuric acid requiring 1.9 c.c. N/5 soda for neutralisation.  $\text{S} = 8.11$  per cent.

$\text{C}_{15}\text{H}_{10}\text{O}_7\text{H}_2\text{SO}_4$  requires  $\text{S} = 8.0$  per cent.

The colouring matter in the first case was collected on a tared filter, washed, dried at  $110^\circ$ , and weighed.

0.112 gave 0.0849 colouring matter = 75.803 per cent.  $\text{C}_{15}\text{H}_{10}\text{O}_7\text{H}_2\text{SO}_4$  requires 75.5 per cent.

*Action of Acetic Anhydride.* — About 1 gram of the colouring matter was heated on the water bath for about 2 hours with 4 c.c. of acetic anhydride and some anhydrous sodium acetate; the mixture was then poured into excess of water, the precipitate collected, and after repeatedly washing with water, was dissolved in hot alcohol, the solution decolorised with charcoal, and set aside. On cooling, the substance crystallised out in silky masses of long needles, which, after recrystallisation from alcohol, melted at  $192^\circ$ ; pentacetylquercetin melts at  $192^\circ$ .

It was analysed by dissolving it in a mixture of sulphuric and acetic acids, precipitating with water, and weighing the colouring matter which separated on cooling.

0.1586 acetyl derivative gave 0.093 colouring matter = 58.65 per cent. Acetylquercetin,  $C_{15}H_5O_7(C_2H_3O)_5$ , requires 58.98 per cent.

*Action of Fused Potash.*—About 0.5 gram of the colouring matter was heated with 10 grams of potassium hydroxide dissolved in 5 c.c. of water for about 20 minutes. The dark chocolate-brown "melt" was dissolved in water, neutralised with dilute sulphuric acid, and extracted with ether; the ethereal solution was distilled, the residue dissolved in water, and after the solution had been decolorised with animal charcoal, lead acetate was added, and the white precipitate thus formed was collected, decomposed with dilute sulphuric acid, and the mixture extracted with ether. The ethereal solution deposited colourless crystals melting at  $192^\circ$ , and an aqueous solution gave a green coloration with solution of ferric chloride. It was therefore *protocatechuic acid* (m. p.  $193^\circ$ ).

The filtrate from the lead acetate precipitate was mixed with dilute sulphuric acid, the mixture extracted with ether, the latter distilled off, and the residue dissolved in water; this solution contained *phloroglucinol*, as, on the addition of hydrochloric acid, it stained a pine shaving a deep magenta colour.

*Methylation of the Colouring Matter.*—The methylic ether of the colouring matter was obtained by boiling a solution in methylic alcohol with potash and methylic iodide for about 15 hours on the water bath; the excess of methylic iodide was then removed by distillation, the residue boiled with benzene, the solution filtered, and the benzene distilled off. The residue, on crystallisation from hot methylic alcohol, gave a mass of glistening, yellow needles melting at  $156^\circ$ ; quercetin methyl ether melts at  $157^\circ$ .

	Formula from combustions.	Acetyl derivative.	Potash fusion products..	Methyl ether.	Composition of $H_2SO_4$ compound.
Colouring matter of <i>Podophyllum emodi</i>	$C_{15}H_{10}O_7$	m. p. $195^\circ$ col. matt. = 58.65 per cent.	protocatechuic acid and phloroglucinol	m. p. $156^\circ$	S=8.196 per cent. col. matter = 75.803 per cent. orange rosettes
Quercetin (from quercitron bark)	$C_{15}H_{10}O_7$	m. p. $195^\circ$ col. matt. = 58.98 per cent.	protocatechuic acid and phloroglucinol	m. p. $158^\circ$	S=8 per cent. col. matter = 75.5 per cent. orange rosettes

This experimental evidence leaves no doubt that the yellow colouring matter of the rhizome of *Podophyllum emodi* is *quercetin*.

These facts tabulated as page 220.

Professor Hummel kindly undertook to ascertain the value of *Podophyllum emodi* as a dye-stuff. He has compared it with quercitron bark and states that the results are most satisfactory. It is therefore probable that this plant will prove to be of commercial value as a dye-stuff and as a source of the dye *quercetin*, in addition to *podophyllin*.

#### *Podophyllo-resin.*

The physiological action of the resin left after exhaustion of 'podophyllin' with chloroform and with ether showed that it still contained some substance which was very active as a purgative, although all the podophyllotoxin had been removed. The only solvent for this resinous residue was alcohol, and by fractional precipitation of such a solution with water, it was found possible to separate the residue into two fractions, one a soft, transparent, brownish-red resin, and the other a black powder almost insoluble in alcohol and containing calcium and magnesium. The former of these two was found to be active as a purgative, and has been named provisionally *podophyllo-resin*, whereas the latter is quite inert. All attempts to isolate a crystalline substance from podophyllo-resin failed, and as it was impossible to ensure its homogeneity, attention was turned to its derivatives in the hope of obtaining some crystalline substance which could be purified, and the analysis of which could be utilised for the determination of the composition of the active resin.

*Action of Acetic Anhydride on Podophyllo-resin.*—About 0.5 gram of resin was boiled for about an hour with acetic anhydride and sodium acetate, the mixture poured into excess of water, allowed to stand for some hours, and the precipitate after being collected and washed with water, was dissolved in boiling alcohol, the solution decolorised with animal charcoal, and set aside. On cooling, a white, somewhat gelatinous, precipitate formed which under the microscope was seen to consist of rosettes of crystals; this was recrystallised from alcohol, in which it is sparingly soluble even on boiling. The recrystallised substance melted at 198° and the melting point was not altered by further recrystallisation.

0.1328 gave 0.3023 CO<sub>2</sub> and 0.0667 H<sub>2</sub>O. C = 62.12; H = 5.57.

0.1217 „ 0.2787 CO<sub>2</sub> „ 0.0560 H<sub>2</sub>O. C = 62.44; H = 5.09.

Mean C = 62.28; H = 5.33. C<sub>16</sub>H<sub>18</sub>O<sub>6</sub> requires C = 62.7; H = 5.8 per cent.

The amount of acetic acid produced on hydrolysis was determined. For this purpose, after a weighed quantity had been boiled with N/10



soda solution for several hours, it was acidified with dilute sulphuric acid, and the acetic acid distilled off.

0.1251 acetyl derivative gave 0.0474 acetic acid = 38.6 per cent.

$C_{12}H_{10}O_4(C_2H_3O)_2$  requires 39.4 per cent.

The resin therefore probably has the formula  $C_{12}H_{12}O_4$  or  $C_{12}H_{10}O_2(OH)_2$ .

*Action of Fused Potash on Podophyllo-resin.*—About 0.3 gram of the resin dissolved in 5 grams of potash and 2 c.c. of distilled water was heated for half an hour; the melt was then dissolved in water, neutralised with dilute sulphuric acid, and the mixture shaken with ether. The ethereal solution was distilled, the residue dissolved in boiling water, and lead acetate solution added; the white precipitate thus formed was decomposed by dilute sulphuric acid, the mixture shaken with ether, and the ether removed by distillation, when a residue was obtained which became crystalline after a time. This residue, when dissolved in water, gave a green coloration with ferric chloride, and therefore contained *protocatechuic acid*, but the recrystallised residue melted at  $200^\circ$  (*protocatechuic acid* melts at  $193^\circ$ ). It was therefore probable that some other substance was present, and in order to determine what this was, a larger quantity (about 2 grams) of the resin, which, however, was not quite so pure as the specimen first experimented with, was fused with potash; the crystalline residue in this case was separated into two fractions, one melting at  $210^\circ$  and the other at  $192^\circ$  (*protocatechuic acid*). Enough of the former could not be obtained for analysis, but the melting point, and the fact that it gives no coloration with ferric chloride solution and is precipitated by bromine water, makes it probable that it is *parahydroxybenzoic acid* (m. p.  $210^\circ$ ). The presence of this substance has already been noted among the products of the decomposition of podophyllin by fused potash (Guareschi, *Ber.*, 1879, 12, 683).

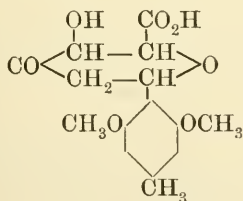
#### *Constituents of Podophyllum peltatum.*

The whole of the work described above in connection with *Podophyllum emodi* has been repeated with the rhizome of *Podophyllum peltatum*. The constituents of the two plants are identical, but the proportions in which they occur differ considerably. Thus, estimation of the amount of the crude substance 'podophyllin' contained in the two rhizomes shows that the American rhizome may contain from 4 to 6 per cent. and the Indian rhizome from 10 to 12 per cent. These results are referred to in the last section of the paper.

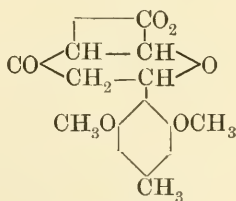
*Constitution of Podophyllotoxin, Picropodophyllin and Picropodophyllic Acid.*

The facts which have been recorded make it possible to discuss the constitution of podophyllotoxin, picropodophyllin and podophyllic acid. There is little doubt that podophyllotoxin and picropodophyllin are isomerides, and that the latter is the lactone or anhydride of podophyllic acid, into which it has been converted and from which it has been obtained. It has been shown that podophyllotoxin, when dissolved in alkalis, passes into a salt of this acid, and that on heating this acid picropodophyllin is produced, which reverts to the acid again when dissolved in alkalis. There is no evidence to show that podophyllotoxin changes into picropodophyllin before it passes into the acid, although this may be suggested as highly probable, since picropodophyllin, and not podophyllotoxin, is formed when the acid is dehydrated. The nature of the isomerism of podophyllotoxin and picropodophyllin is at present obscure; the chief difference between the two compounds is that podophyllotoxin is lævorotatory, whilst picropodophyllin is optically inactive, podophyllic acid is, however, like podophyllotoxin, lævorotatory.

The principal facts which must be represented by any structural formula for podophyllotoxin are (1) the composition expressed by the empirical formula  $C_{15}H_{14}O_6$ , (2) the optical activity, (3) the existence of two methoxyl groups, (4) the hydration by alkalis producing an unstable acid, (5) the formation of a monobromo-derivative, (6) the production of orcinol and acetic acid on fusion with potash, (7) the production of oxalic acid on oxidation with nitric acid. We believe that these facts are satisfactorily represented if podophyllotoxin and its congeners are regarded as the derivatives of a hydrogenated pyronecarboxylic acid. It appears highly probable that podophyllic acid is the carboxylic acid of a *dimethoxymethyl-phenylhydro-γ-pyrone*, of which picropodophyllin is the lactone, whilst podophyllotoxin must have a very similar constitution; possibly it is an optically active form of the racemic lactone. We therefore propose the following formulæ for these substances.



Podophyllic acid.



Picropodophyllin.

Since quercetin accompanies podophyllotoxin in the plant, it is interesting to recall the fact that, according to Herzig and others, quercetin is also a derivative of a phenylated pyrone.

*Estimation of "Podophyllin" and "Podophyllotoxin" in  
P. emodi and P. peltatum.*

*Podophyllin*.—As the rhizome of podophyllum is chiefly used for the preparation of *Resina podophylli* (podophyllin), the estimation of the amount of resin in the rhizome is of some commercial importance.

The process of estimation used consisted in taking a weighed portion of the powdered rhizome, extracting this in a Soxhlet percolator with boiling absolute alcohol, evaporating the percolate to a thin syrup, adding excess of water, and allowing the precipitated resin to settle. The water was then poured off, the process being repeated until the water ceased to extract any sugar. The resin was then dried at 100° and weighed.

The following is a tabular statement of the amounts of resin contained in samples derived from different districts of the Punjab.

District.	Percentage of resin.
Kulu .....	9.55
Bashahr .....	9.003
Chamba { Mature roots .....	11.12
{ Young roots.....	12.03
Hazara .....	9.06

Estimations of resin in four specimens of the rhizome of *Podophyllum peltatum* gave respectively 4.17 per cent., 5.2 per cent., 5.4 per cent., 5.2 per cent. Dymock and Hooper (*loc. cit.*) found 10 per cent. of resin in the Indian rhizome, and Umney (*loc. cit.*) 12 per cent.

*Podophyllotoxin*.—An attempt was first made to estimate directly the amount of podophyllotoxin in podophyllum rhizome by percolation with suitable solvents, but this had to be abandoned owing to the difficulty of purifying the material without loss.

The conversion of podophyllotoxin into its very insoluble and easily purified isomeride picropodophyllin next suggested itself as an indirect method of estimation, and preliminary experiments showed that by taking a weighed quantity of podophyllotoxin and converting it into picropodophyllin by treatment with lime, 98 per cent. of the amount taken could be recovered in the form of picropodophyllin.

The process finally adopted is carried out as follows. A weighed quantity of the ground rhizome dried at 100° is mixed with lime, and the mixture percolated with chloroform in a Soxhlet extraction apparatus, the residue left on evaporating the chloroform

solution to dryness is dissolved in absolute alcohol, the solution made into a thin paste with slaked lime, and the whole evaporated to complete dryness; more alcohol is then added, and the process repeated. The dried residue is then mixed with absolute alcohol, the mixture boiled and filtered through a jacketed funnel, and the residue and the filter paper containing it, after being allowed to dry somewhat, is packed into an extraction apparatus, percolated with alcohol, and the percolate mixed with the original alcoholic filtrate; the mixed liquids are then evaporated to dryness in a tared dish and the residue of picropodophyllin weighed. The residue thus obtained is almost colourless and is usually well crystallised, but contains a small quantity of calcium picropodophyllate due to incomplete dissociation of the salt during the drying of the chloroform extract with lime. On incineration, the residue gives on an average about 1 per cent. of calcium oxide, but as this is responsible for only a very small error in an estimation, it may be neglected.

The following table includes the results of a series of estimations of podophyllotoxin in Indian and American podophyllum, and for convenience of comparison the percentages of resin (podophyllin) are also given.

District yielding the specimens.	Quantity of rhizome used.	Percentage of podophyllotoxin found.	Percentage of resin found.	
Kulu .....	11.92 grams	2.8	9.55	} <i>Podophyllum emodi.</i>
	15.17	2.9		
Bashahr .....	32.46	3.5	9.00	
	27.12	3.6		
Chamba. ....	10.97	5.17	3	} <i>Podophyllum emodi.</i>
Young roots...	13.46	5.3		
Old roots .....	9.81	4.7	11.12	
	10.59	4.51		
Hazara .....	11.6	2.9	—	} <i>Podophyllum peltatum.</i>
	14.5	3.08		
United States of America	11.35	0.77	5.2	
	12.02	0.82		
	23.55	0.995	4.17	} <i>Podophyllum peltatum.</i>
	22.6			

Taking the average yield of resin and of crystallised podophyllotoxin from the rhizome of *Podophyllum emodi* to be 10 per cent. and 3.5 per cent. respectively, the amount of podophyllotoxin in podophyllin from the Indian drug must be about 38 per cent., whilst that contained in American podophyllin is only about 20 per cent., although in extracting podophyllotoxin itself from the plant nothing like this quantity is obtained, owing to the difficulty experienced in purifying it from the

viscous resinous substances also removed by the solvents. Although there is a difference of nearly 20 per cent. in the amount of podophyllotoxin contained in the podophyllin from these two sources, it is remarkable that they differ comparatively little in physiological activity, a fact which supports the view that podophyllotoxin cannot be regarded as the only active constituent of the resin.

Since the Indian resin contains more podophyllotoxin than the American, it behaves somewhat differently when warmed with alkalis, owing to the larger amount of the insoluble picropodophyllin which is formed and crystallises out. The test of the British Pharmacopœia, which requires podophyllin to be soluble in aqueous ammonia, therefore needs modification. In preparing the ammoniacal tincture from the Indian resin, the mixture should not be heated. Nor, indeed, should heat be used in any case in preparing the tincture, since even with the American resin some of the active podophyllotoxin will be changed into the inert picropodophyllin.

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## XVI.—*The Volatile Constituents of the Wood of Goupia tomentosa.*

By WYNDHAM R. DUNSTAN, F.R.S., and T. A. HENRY, Salters' Research Fellow in the Laboratories of the Imperial Institute.

*Goupia tomentosa* is a large tree growing in British Guiana, where it is known as "Kabucalli," and used in the colony for boat-building; it has recently been sent with other timbers by the Government of the Colony to the Scientific Department of the Imperial Institute, so that its general merits as a timber might be ascertained. The timber has been submitted to mechanical tests by Professor Unwin, F.R.S., in the course of an examination of the various timbers of British Guiana which he has conducted for the Imperial Institute. An account of these tests has been published (*Imperial Institute Journal*, 3, p. 51).

When the log sent from the colony was cut, the wood was seen to be reddish, very hard, with a fine, close grain. When first cut, it emitted a strong odour resembling that of valeric acid, and when shaved with a plane, the cut surface became covered with a thin film of oil. On account of these peculiarities, it was decided to examine its chemical constituents; for this purpose, the wood was cut up into fine shavings, which were at once placed under water, and, after standing about



12 hours, were steam distilled. The distillate was then concentrated by steam distillation, and the process repeated until fatty particles began to separate from the distillate; the liquid was now shaken with ether, and the ethereal solution dried with calcium chloride and distilled. In this way, a dark-coloured oil was obtained, which became semi-solid on cooling; this was dissolved in boiling alcohol, and decolorised with animal charcoal; on cooling, the filtered solution deposited a colourless, fatty substance, which was obtained in small needles by repeating the process. When pure, it melted at  $45^{\circ}$ ; it distilled under reduced pressure, and was slowly dissolved by alkaline solutions, and reprecipitated from them by acids. A combustion of the pure material gave the following result.

0.1624 gave 0.4281  $\text{CO}_2$  and 0.1783  $\text{H}_2\text{O}$ .  $\text{C} = 72.04$ ;  $\text{H} = 12.19$  percent.

*Lauric acid*,  $\text{C}_{12}\text{H}_{24}\text{O}_2$  requires  $\text{C} = 72$ ;  $\text{H} = 12$  per cent.

A sodium salt was prepared by exactly neutralising an alcoholic solution of the acid with alcoholic soda and evaporating the solution in a vacuum desiccator over potash. A white precipitate slowly separated, and this, on analysis, gave the following result.

0.142 gave 0.0450  $\text{Na}_2\text{SO}_4$ .  $\text{Na} = 10.2$  per cent.

$\text{C}_{12}\text{H}_{23}\text{O}_2\text{Na}$  requires  $\text{Na} = 10.4$  per cent.

The substance therefore agrees in composition and properties with *lauric acid* (m. p.  $43.6^{\circ}$ ).

This acid occurs, usually as the glyceride, in many plants, but notably in the oils obtained from the fruit of *Laurus nobilis* and *Cocos nucifera*. As lauric acid is only slightly volatile in steam, its isolation by steam distillation is extremely tedious, and having identified it, an attempt was made to obtain it by extracting the wood shavings with ether; this, however, was not found to be feasible, owing to the large amount of resin also removed by the ether, and from which it is very difficult to isolate the lauric acid by crystallisation.

The aqueous distillate left after extraction with ether was made strongly alkaline with solution of soda, evaporated to dryness over the water bath, and then acidified with dilute sulphuric acid; the oil which separated was removed by ether, the ethereal solution dried with calcium chloride, the ether distilled off, and the residue fractionated several times; in this way, three fractions were obtained, boiling respectively at about  $46^{\circ}$ ,  $150^{\circ}$ , and  $206^{\circ}$ .

The first of these fractions was very small; it had a pungent odour, and its aqueous solution reduced silver nitrate and mercuric chloride. It probably, therefore, contained *formic acid*, but enough could not be obtained for complete identification.

The fraction boiling at about  $150^{\circ}$  was dissolved in dilute soda

solution and the solution evaporated; two fractions of crystalline sodium salt were obtained. These were converted into the silver salts, the second fraction of sodium salt being precipitated in two portions with silver nitrate; the silver salts, on analysis, gave the following numbers.

First fraction of sodium salt gave a silver salt containing 48.6 per cent. Ag.

Second fraction of sodium salt gave two fractions of silver salt, A and B. A, containing 49.9 per cent. Ag; B, containing 50.6 per cent. Ag.

In a second experiment, in which a larger amount of sodium salt was obtained, the crystals were separated into two fractions, and these again fractionated by addition of silver nitrate solution; the first fraction of silver salt contained 48.3 per cent. Ag. From the results of these analyses, and the properties of this fraction of oil, it evidently consists of a mixture of *isovaleric* and *caproic acids*.

Silver isovalerate requires 51.4 per cent. Ag.

Silver caproate requires Ag = 48.2 per cent.

The fraction of oil boiling at 206°, which constituted about 60 per cent. of the whole, had all the properties of *normal hexoic (caproic) acid*, but it was not quite pure, since on conversion into the sodium salt and fractional precipitation of the solution of this salt with silver nitrate, some fractions containing 56 to 58 per cent. of silver were obtained, but the greater portion of salt contained 47.82 per cent. of silver. The oil was therefore redistilled very slowly, and the first portion, which boiled almost constantly between 206° and 209°, collected. Normal caproic acid boils at 206°, and silver caproate contains 48.2 per cent. of silver.

The oily residue left after the redistillation of the second fraction of oil became coloured on further heating, and it was strongly acid to litmus. The residue was dissolved in ether, decolorised by animal charcoal, and the ether distilled off; the oil, on being allowed to stand for some months, deposited a small quantity of a crystalline substance. These crystals were removed, dried first on a porous tile and then at 100°. The substance melted at 180°, and sublimed when heated gently in a test tube; it was acid to litmus. The whole of the material obtained was converted into the silver salt, and the latter ignited, with the following result.

0.0082 gram gave 0.0051 Ag. Ag = 62.2 per cent.

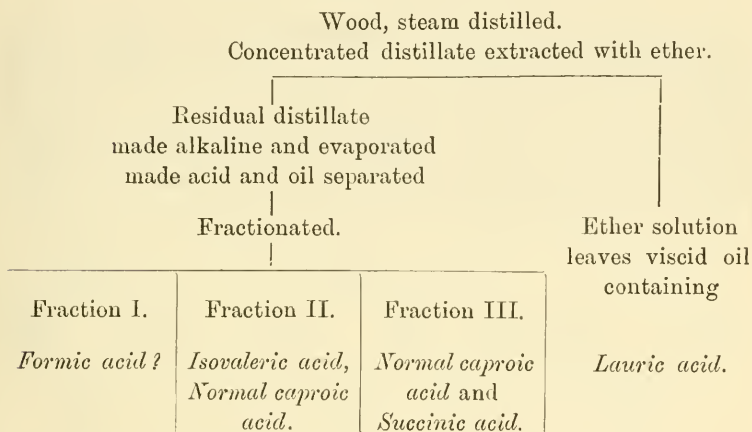
Silver succinate requires Ag = 64.4 per cent.

This agreement is as good as can be expected, since the quantity

available for analysis was so small that a difference of one unit in the fourth decimal place causes an error of 1 per cent. in the result.

The properties of the substance leave little room for doubt that it is *succinic acid* (m. p. 180°).

SUMMARY OF SEPARATION OF CONSTITUENTS.

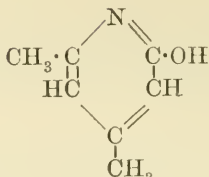


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XVII.—*Production of some Nitro- and Amido-oxy-lutidines. Part I.*

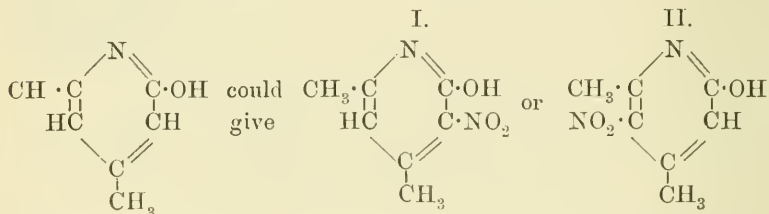
By PROF. J. N. COLLIE, Ph.D., F.R.S., and THOMAS TICKLE, Salters' Company's Research Fellow in the Research Laboratory of the Pharmaceutical Society of Great Britain.

In a former paper (Trans., 1897, 838), one of the authors has drawn attention to the fact that nitro- and amido-derivatives of pyridine can be obtained from oxypyridine compounds by the ordinary process of nitration and reduction. As these substances correspond in the pyridine series to nitro- and amido-phenols in the benzene series, their reactions and properties are of some interest, and it has been considered worth while to continue the investigation, using a hydroxylutidine (pseudolutidostyryl) as the starting point.

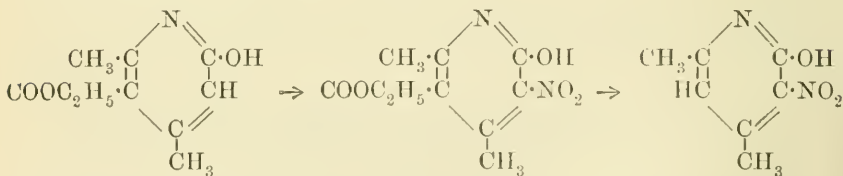


Pseudolutidostyryl.

This compound,  $\alpha\gamma$ -dimethyl- $\alpha'$ -hydroxypyridine, is easily nitrated when treated with a mixture of strong nitric and sulphuric acids, yielding a nitropseudolutidostyryl, which, on reduction with tin and hydrochloric acid, gives an amidolutidostyryl. As, however, the entering nitro-group might replace either of two different hydrogen atoms, it was necessary to determine if possible the exact composition of the new nitro-derivative.

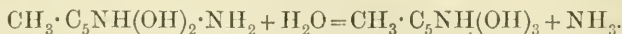


That the substance had the molecular structure represented by the formula I. was proved by obtaining it from ethylic nitrolutidostyryl-carboxylate (Trans., 1897, 71, 301).



When this nitrohydroxylutidine is subjected to the reducing action of tin and hydrochloric acid, it is at once converted into the corresponding amidohydroxylutidine.

In a former paper by one of the authors (Trans., 1897, 71, 842), an amidodihydroxypicoline was similarly prepared, and it was then noticed that the dioxy-compound suffered a somewhat curious change when boiled, passing into a trihydroxypicoline:—

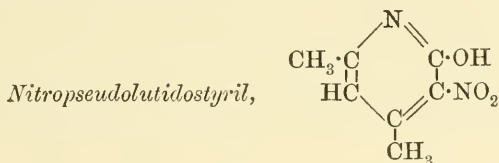


This reaction is different from any that amidophenols undergo, but is similar to the formation of orthonitrophenol from orthonitr-aniline when the latter is boiled with alkalis; possibly it may be due

to the ease with which, in  $\alpha$ -hydroxypyridine compounds, the ring binding can be loosened and opened out (Trans., 1897, 71, 839).

We were in hopes, that as the amido-group and the hydroxy-group in the amidohydroxylutidine were in the same relative positions (namely,  $\alpha$  and  $\beta$ ), the same reaction might again occur, and the corresponding dihydroxylutidine derivative be formed, but although many attempts were made no such change could be effected.

The amidohydroxylutidine is a substance with characteristic properties, it is very unstable and cannot be heated to  $100^\circ$  without turning brown; it rapidly reduces solution of nitrate of silver and platonic chloride. With ferric chloride, it gives first a red and then a bright green coloration, but it does not yield the series of brilliant colour reactions in alkaline solution like the trihydroxypicoline mentioned above (Trans., 1897, 71, 843). When, however, it is dissolved in strong sulphuric acid and a drop of nitric acid is added, a strong purple coloration is produced similar to that which strychnine gives when treated with sulphuric acid and potassium dichromate.



The pseudolutidostyryl employed was prepared from ethylic  $\beta$ -amido-crotonate according to the method given in a former paper by one of the authors (Trans., 1897, 71, 299); it was found convenient only to nitrate small quantities of the substance at a time. Three to four grams of the pseudolutidostyryl were dissolved in 6 c.c. of sulphuric acid, and this mixture was then slowly added to 8 c.c. of a mixture of sulphuric and fuming nitric acids, which were kept well cooled: large quantities are less easily manageable, the temperature being liable to rise suddenly, when the whole of the substance is destroyed by oxidation. The mixture is then diluted with 10 times its volume of water, the new nitro-derivative which separates in yellow needles being most conveniently recrystallised from 30 per cent. acetic acid, or a mixture of 30 per cent. acetic acid to which about 3 per cent. of nitric acid has been added. When pure, it crystallises in light yellow needles that melt somewhere about  $250^\circ$  if suddenly heated to that temperature, but if the heating be slow, the crystals darken at about  $243^\circ$  and then rapidly decompose. On analysis, the following numbers were obtained:

	C.	H.	N.
Found.....	49.8	5.4	17.5
Calculated for $\text{C}_7\text{H}_8\text{N}_2\text{O}_3$ .....	50.0	4.8	16.7



No other nitro-compound seemed to be present, and the only substance produced by the nitration of pseudolutidostyryl was the compound mentioned above. It is not volatile with steam, and with alkalis, it gives brilliant yellow compounds.

*Amidopseudolutidostyryl*,  $C_5NH(CH_3)_2(OH) \cdot NH_2$ .

When the nitro-derivative of pseudolutidostyryl is reduced with tin and hydrochloric acid, the hydrochloride of amidopseudolutidostyryl is formed, the reaction being accompanied by a considerable evolution of heat. After precipitating the tin by means of hydrogen sulphide, the solution is evaporated on the water bath, when the hydrochloride of the base begins to separate as soon as the solution becomes concentrated. A second method for preparing the hydrochloride was used; if, after the reduction with tin and hydrochloric acid, the solution is evaporated, a well crystallised double salt of the hydrochloride of amidopseudolutidostyryl and tin chloride separates; this can be purified and then its solution decomposed by means of hydrogen sulphide. By either method, a white salt was obtained crystallising in needles, and decomposing without melting at  $235-240^\circ$ , but like the nitrolutidostyryl, if suddenly heated to about  $300^\circ$ , it can be partially melted before decomposition ensues. It was analysed.

	C.	H.	N.	Cl.
Found .....	47.8	6.4	20.3	19.6
Calculated for $C_7H_{10}N_2O, HCl$	48.1	6.3	20.3	20.3

The substance, therefore, is a monhydrochloride.

When this hydrochloride is treated in aqueous solution with sodium hydrogen carbonate, it is converted into the free base, which is less soluble and separates in the form of a bulky mass of fine, needle-shaped crystals; these were purified by recrystallisation from water until they melted constantly at  $205^\circ$  (corr.). The base is very soluble in hot water but less so in cold (to the extent of 8—10 per cent. in cold), it is very unstable at  $100^\circ$ , the dry substance rapidly turning brown when heated in a water oven to that temperature. The aqueous solution even turns brown on boiling, and in the presence of alkalis the decomposition is much more rapid.

When added to a cold solution of silver nitrate, it instantly gives a black precipitate of silver, and when warmed with a little chloride of platinum reduction was found to take place; the normal platinochloride can be prepared, but in the presence of hydrochloric acid it changes into a new salt containing 3 per cent. more platinum than the normal salt. This new salt was produced when trying to recrystallise the ordinary salt from dilute hydrochloric acid.

Analyses of both salts were made.

The normal platinochloride contained 28.5 per cent. Pt.

Calculated for  $(C_7H_{10}N_2O)_2, H_2PtCl_6$  28.4 per cent. Pt.

The new salt obtained from hydrochloric acid solution, on analysis, was found to give the following numbers.

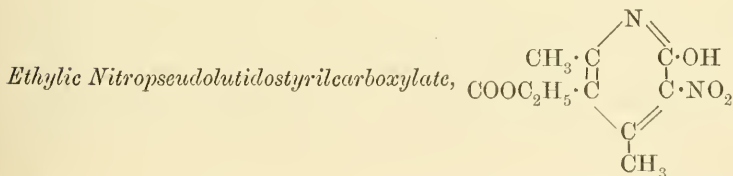
	C.	H.	Pt.	Cl.
Found .....	20.4	3.0	31.5	34.8
Calculated for	20.4	2.7	31.5	34.5
$(C_7H_{10}N_2O)_2, H_2PtCl_6$				
$C_7H_{10}N_2O, H_2PtCl_6$				

This substance appears therefore to be a compound of the mono- and the di-hydrochlorides of the base with platinic chloride.

When the amidopseudolutidostyryl is heated on the water bath with acetic anhydride, it is converted into a monacetyl derivative which can be crystallised either from water or from alcohol. It is obtained in white, silky needles melting at  $255^\circ$  (corr.), it is neutral to litmus paper, and fairly soluble in cold, but very soluble in hot, water. Ether, acetone and ethylic acetate dissolve it more sparingly, and it differs from amidopseudolutidostyryl in that it gives no reaction with ferric chloride, neither does it reduce silver nitrate solution. The amidopseudolutidostyryl can be regenerated from it by hydrolysis with dilute hydrochloric acid heating the mixture under pressure in a sealed tube.

It gave the following numbers on analysis.

	C.	H.
Found .....	60.1	6.5
Calculated for $C_7H_9N_2O, C_2H_3O$	60.0	6.6



This is produced when ethylic pseudolutidostyrylcarboxylate (m. p.  $138-139^\circ$ ) is nitrated in the ordinary manner with a mixture of strong nitric and sulphuric acids. It is scarcely soluble in water, but can be recrystallised from acetic acid; it then forms long, pale yellow, needle-shaped crystals, which melt without decomposition at  $215^\circ$  (corr.). It was analysed.

	C.	H.	N.
Found .....	49.7	6.1	11.6
Calculated for $C_{10}H_{12}N_2O_5$ .....	50.0	6.0	11.6

It is not very soluble even in hot soda solution, but, on warming, decomposition slowly occurs and the brilliant yellow sodium salt of the nitropseudolutidostyrylcarboxylic acid is produced.

This nitropseudolutidostyrylcarboxylic acid was also prepared in larger quantities by nitrating the free acid. Ten grams of the acid were carefully added to 20 c.c. of well cooled fuming nitric acid, and afterwards poured into 10—15 c.c. of strong sulphuric acid; care must be taken not to allow the temperature to rise, otherwise a violent action begins, and the substance is entirely destroyed.

On pouring the mixture into cold water, the new nitro-acid separates. It was found on analysis to contain  $1\text{H}_2\text{O}$ .

Loss of weight at  $100^\circ = 8.2$  per cent.

Calculated for  $\text{C}_8\text{H}_8\text{N}_2\text{O}_5 + \text{H}_2\text{O} = 7.8$  per cent.

The dried substance gave the following numbers.

	C.	H.	N.
Found .....	45.3	4.2	13.3
Calculated for $\text{C}_8\text{H}_8\text{N}_2\text{O}_5$ .....	45.3	3.8	13.2

This nitro-acid can be recrystallised from acetic acid or water, but it is not very soluble in the latter. When pure, the crystals are almost white needles, the aqueous solution having only a faint yellowish tint; when rapidly heated, they melt at  $260^\circ$  (corr.). The ammonium salt is easily obtained in the crystalline condition, and is bright yellow; it gives a brown precipitate with ferric chloride, and a crystalline precipitate with silver nitrate. The lead and barium salts seem to be soluble.

The moment the free acid is melted, it effervesces and evolves carbon dioxide, whilst a yellow, crystalline residue remains which melts at a temperature  $10\text{--}15^\circ$  below the acid; after purification, this residue was found to be identical with the nitropseudolutidostyryl obtained by nitrating pseudolutidostyryl itself and already mentioned earlier in this paper. This method for the manufacture of nitropseudolutidostyryl was not used, because the decomposition of the substance at the temperature at which the nitro-acid fused was very considerable.

*Amidopseudolutidostyrylcarboxylic acid*,  $\text{NH}_2 \cdot \text{C}_5\text{N}(\text{CH}_3)_2(\text{OH}) \cdot \text{COOH}$ .

When the nitro-acid is reduced by means of tin and hydrochloric acid, the hydrochloride of the corresponding amido-derivative is produced. To prepare this substance, the nitro-acid is dissolved in strong hydrochloric acid, and the tin is added little by little, the reduction taking place very readily with a considerable rise of temperature. The acid solution obtained after the tin has been precipitated with hydrogen

sulphide is evaporated on the water bath, and from the concentrated solution the hydrochloride separates in needle-shaped crystals; these can be recrystallised from hydrochloric acid, but with pure water the substance is decomposed into the free acid, which is much more insoluble than the hydrochloride.

The hydrochloride gave the following results on analysis.

	C.	H.	N.	Cl.
Found .....	37.9	6.0	11.3	14.0
Calculated for $C_8H_{10}N_2O_3 \cdot HCl + 2H_2O$	37.7	5.9	11.0	13.9

The substance, when heated at  $100^\circ$ , lost 14.5 per cent.  $H_2O$ .

The calculated amount corresponding with  $2H_2O = 14.1$  per cent.

The amido-acid can be prepared by decomposing the hydrochloride with excess of water; it is very slightly soluble even in hot water. From hot alcohol it separates in needles, whilst if the potassium salt be decomposed by acetic acid the free acid can be obtained in the form of small flat prisms; it is insoluble in ether, acetone, and chloroform. It is unstable, turning brown rapidly when heated to  $100^\circ$ ; the alcoholic and aqueous solutions behave in a similar manner.

The amido-acid has strong reducing properties; if added to silver nitrate solution, it forms a dense grey precipitate of silver, and the solution becomes pale green. With ferric chloride, it gives a pale green coloration which rapidly deepens to emerald green, purple, and finally deep blue. With ferrous sulphate, it gives no coloration, and the calcium, barium, lead, and copper salts seem to be soluble.

When very carefully heated on an oil bath, the acid melts at  $275^\circ$  (corr.). It also loses, at  $100^\circ$ , 8.7 per cent. of water.

Calculated for  $C_8H_{10}N_2O_3 + H_2O$ ;  $H_2O = 9.0$  per cent.

At its melting point, it gives off carbon dioxide, and the residue (which sublimes at the temperature at which the decomposition occurs), after purification, was found to melt at  $205^\circ$  (corr.); its hydrochloride melted at about  $300^\circ$ , and corresponded in all respects with the amidopseudolutidostyryl obtained by the reduction of the nitropseudolutidostyryl.

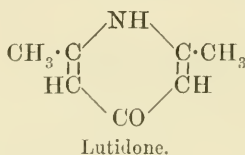
### XVIII.—*Production of some Nitro- and Amido-oxy lutidines. Part II.*

By Miss L. HALL (University College, London) and J. NORMAN COLLIE, Ph.D., F.R.S. (Professor of Chemistry at the Pharmaceutical Society of Great Britain, London).

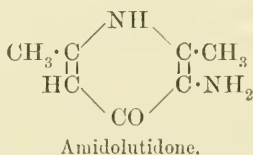
THE production of nitro- and amido-derivatives in the pyridine series has been the subject of two former papers communicated by one of the authors to the Society (Trans., 1897, 71, 838 and 1898, 229). In

the first of these papers, it was shown that, when dioxypicoline is dissolved in nitric acid, nitration at once occurs, and from the nitro-dioxypicoline produced, several amido- and oxy-picoline derivatives could be prepared. The present communication is a continuation of that work.

The oxy-pyridine derivative chosen was lutidone, or *aa'*-dimethyl- $\gamma$ -oxy-pyridine.



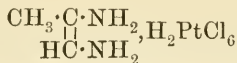
It was found that lutidone, however, was not nitrated when treated with nitric acid alone, as was the case with the di-oxy-picoline, but was only converted into the nitrate of lutidone, and a mixture of fuming nitric and sulphuric acids had to be employed before it was changed into nitrolutidone. This was the case also with pseudolutidostyryl (Trans., 1898, 230). The nitrolutidone is a very pale yellow, crystalline compound which dissolves in alkalis with an intense yellow colour, has a strong acid reaction, and is not volatile with steam. When treated with tin and hydrochloric acid, it is easily reduced, forming an amidolutidone.



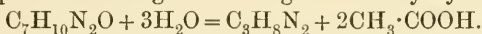
This amidolutidone, unlike amidodioxypicoline and amidopseudolutidostyryl, does not give characteristic colours when treated with various oxidising agents, this being probably due to the fact that the amido- and the oxy-group are in the ortho-position relatively to one another. It does, however, yield a brownish-red coloration with ferric chloride, but with strong sulphuric acid and potassium dichromate or with nitric acid no marked coloration is produced. It has, however, strong reducing properties; with nitrate of silver, it gives first a white, semi-crystalline precipitate which is entirely reduced to metallic silver on warming. It also forms two hydrochlorides, a mono- and a di-derivative, and its platinochloride belongs to the class of double salts where 1 mol. of the dihydrochloride unites with 1 mol. of platinic chloride. This platinochloride is very unstable, and when dissolved in water and warmed undergoes reduction, but if its solution be warmed with hydrochloric acid, another kind of change ensues and an exceedingly



insoluble platinochloride separates, which, from its analysis, seems to be the salt of propine-diamine.



The decomposition having been brought about by hydrolysis,



This breaking down of the pyridine ring is one of considerable interest, and in a substance like lutidone was hardly to be expected, for the nitrogen atom is bound to two carbon atoms neither of which are united to oxygen, and lutidone is not the anhydride of an amido-acid as is the case of pseudolutidostyryl.

#### EXPERIMENTAL.

##### *αα'-Dimethyl-γ-oxy-β-nitropyridine.*

The lutidone used in the following experiments was prepared from dehydracetic acid by heating it in sealed tubes at 130° with excess of strong aqueous ammonia, the product being a mixture of lutidone and ammonium lutidonecarboxylate. By evaporating the contents of the tubes to dryness and subsequent distillation crude lutidone was obtained; this was recrystallised from water until pure.

A large number of attempts were made to nitrate lutidone, at first with nitric acid alone, it having been found in the case of dioxypicoline to give almost quantitative yields of the nitro-derivative. A very soluble nitro-compound was obtained which decomposed rapidly at 85°. After it had been recrystallised from water, several analyses were made, but although these agreed amongst themselves, yet, as soon as the substance was recrystallised from alcohol or acetic acid, the analytical numbers showed that, with each solvent, a different change was being effected, and it was not until the compound was purified by recrystallisation from nitric acid that any results were obtained which could be relied upon.

Found C = 45·4 and 44·9; H = 5·7 and 5·8; N = 15·2 and 15·2.

Calculated for  $\text{C}_7\text{H}_{10}\text{N}_2\text{O}_4$ , C = 45·2; H = 5·3; N = 15·1 per cent.

The substance melted at 120° when quickly heated to that temperature, but if kept at 100° it decomposed. Attempts were made also to reduce it with tin and hydrochloric acid, and a crystalline hydrochloride was obtained, but this hydrochloride did not seem to possess the properties of an amido-oxypyridine derivative, neither did the original nitrolutidone yield yellow salts with soda or potash. Ultimately, it was found that the supposed nitro-compound was merely the nitrate of lutidone, for when neutralised with the proper quantity of caustic soda and the solution evaporated, unchanged

lutidone was recovered together with sodium nitrate; moreover, the original substance gave, with strong sulphuric acid and ferrous sulphate solution, the ordinary nitrate test, whilst the supposed hydrochloride of amidolutidone gave results agreeing with lutidone hydrochloride, and lutidone was actually prepared from it by treatment with soda solution.

Found N = 8.7; Cl = 22.3 per cent.

Calculated for  $C_7H_9NO, HCl, H_2O$ , N = 8.7; Cl = 22.0 per cent.

The supposed nitrolutidone was, therefore, merely lutidone nitrate,  $C_7H_{10}N_2O_4 = C_7H_9NO, HNO_3$ .

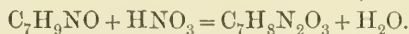
Not having been able to prepare a nitro-derivative by the action of nitric acid alone, a mixture of nitric and sulphuric acids was next tried. Twenty grams of lutidone was dissolved in 30 c.c. of strong sulphuric acid and 60 c.c. of a mixture of equal volumes of fuming nitric and sulphuric acids was added; no nitrous fumes were evolved. It was then warmed for a few moments on a water bath and when cold poured into water, and the aqueous solution nearly neutralised with sodium carbonate, pale yellow crystals at once began to separate; these, which were nearly soluble in cold water, were washed and recrystallised from dilute acetic acid. When pure, they are nearly colourless, having only a faint yellowish tinge. The compound melts at about 290—300° with considerable decomposition. It has a strong acid reaction, and when dissolved in soda yields a brilliant yellow solution; the yellow solution obtained by dissolving the substance in ammonia gradually loses its colour when boiled, the unchanged nitro-derivative ultimately crystallising out after all the ammonia has been driven off. This ammoniacal solution gives a brilliant yellow precipitate with silver nitrate solution.

On analysis, the following numbers were obtained.

Found C = 49.9 and 49.8; H = 5.1 and 5.2; N = 16.7 and 16.9.

Calculated for  $C_7H_8N_2O_3$ , C = 50.0; H = 4.7; N = 16.6 per cent.

The compound is therefore the true nitrolutidone,



*αα'-Dimethyl-γ-oxy-β-amidopyridine.*

When nitrolutidone is added to a mixture of granulated tin and strong hydrochloric acid, it at once dissolves and the temperature rises considerably; the reduction is very rapidly effected, and after the tin has been precipitated by hydrogen sulphide, the filtered liquid on evaporation yields crystals of amidolutidone hydrochloride. This salt is best recrystallised from hydrochloric acid; it then forms a granular mass of crystals, which, in solution, have a strongly acid reaction. On

keeping, they lose both hydrochloric acid and water. Some of the substance was dried between filter paper and analysed as soon as dry.

Found  $C = 33.6$  ;  $H = 6.9$  ;  $N = 11.6$  ;  $Cl = 28.4$  per cent.

Calculated for  $C_7H_{10}N_2O, 2HCl, 2H_2O$ ,  $C = 34.0$  ;  $H = 7.3$  ;  $N = 11.4$  ;  $Cl = 28.7$  per cent.

An estimation was also made of the water of crystallisation, but as it loses hydrogen chloride also when heated, the result is possibly not a correct one.

Found (after heating quickly at  $100^\circ$ )  $H_2O = 15.0$  per cent.

Calculated, 2 mols. of water,  $H_2O = 14.5$  per cent.

The salt melts at about  $275-280^\circ$  (corr.), losing a considerable amount of hydrogen chloride.

When its solution is treated with only one molecular proportion of sodium hydrogen carbonate, a monohydrochloride melting at  $186^\circ$  (corr.) can be obtained ; this, when heated at  $100^\circ$  for some time, decomposes and turns brown. It was recrystallised from alcohol and a nitrogen estimation made.

Found  $N = 16.7$  per cent.

Calculated for  $C_7H_{10}N_2OHCl$ ,  $N = 16.1$  per cent.

Both these hydrochlorides when entirely neutralised by either soda or sodium carbonate, yield amidolutidone which is not very soluble in cold water, and can be easily purified by recrystallisation from water. It crystallises in long, needle-shaped crystals, and when analysed gave the following results.

Found  $C = 52.7$  ;  $H = 7.9$  ;  $N = 17.8$  per cent.

Calculated for  $C_7H_{10}N_2O, H_2O$ ,  $C = 53.8$  ;  $H = 7.7$  ;  $N = 17.9$  per cent.

The substance was also dried at  $100^\circ$  and analysed.

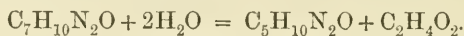
Found  $C = 60.1$  ;  $H = 7.7$ .  $N = 20.6$  per cent.

Calculated for  $C_7H_{10}N_2O$ ,  $C = 60.9$  ;  $H = 7.3$  ;  $N = 20.3$  per cent.

Two determinations of the water of crystallisation were also made. Found  $H_2O = 11.7$  and  $11.5$ . Calculated for  $1H_2O$ ,  $11.5$  per cent.

This amidolutidone, as has already been pointed out, does not yield such a brilliant series of colour tests, when treated with various oxidising reagents, as either the amidodihydroxyppicoline or the amidopseudolutidostyrl. It does, however, give a brownish-red coloration with ferric chloride, and with strong sulphuric acid and solid potassium dichromate a green colour. Its chief characteristic property is its reducing power ; when silver nitrate is added to its aqueous solution, a voluminous, white precipitate is formed at first, but on warming complete reduction occurs, and metallic silver is produced as a

grey metallic deposit, in this respect it resembles the amidodihydroxypicoline. If amidolutidone is persistently boiled with carbonate of soda solution, it is partially decomposed, and some acetate can be detected in the solution, and instead of giving the platinochloride of amidolutidone, another platinum salt was obtained containing 37.5 per cent. Pt. This agrees with  $C_5H_{10}N_2O, H_2PtCl_6$ ; Pt = 37.2 per cent. The decomposition may possibly have occurred as follows,



The true platinochloride of amidolutidone is a very soluble salt, and is best prepared by pouring a strong solution of platinic chloride on to solid amidolutidone hydrochloride. It then crystallises in small, very characteristic, microscopical, shield-shaped crystals; these cannot be recrystallised from hot water, as they entirely decompose when warmed in aqueous solution. They were analysed.

Found Pt = 32.3 and 32.7; water of crystallisation,  $H_2O = 5.9$  per cent.

Calculated for  $C_7H_{10}N_2O, H_2O, H_2PtCl_6 + 2H_2O$ , Pt = 32.4;  $2H_2O = 5.9$  per cent.

When this platinum salt is dissolved in dilute hydrochloric acid and the solution is warmed, a granular platinum salt begins to separate after a short time; this is only sparingly soluble, even in hot water, its hot aqueous solution also, if not acid with hydrochloric acid, undergoes reduction on boiling, and the dry salt, when heated, chars, but does not melt.

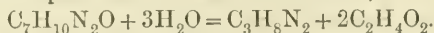
When dried, it contains as much as 40.2 per cent. of platinum, thus showing that it must not only be the platinum salt of a base with a very small molecular weight, but also that the base must belong to the class of diamines. The salt was dried at  $100^\circ$  and analysed.

Found C = 7.2; H = 2.2; N = 5.9; Pt = 40.2, 40.3, 40.5 per cent.

Calculated for  $C_3H_8N_2, 2HCl, PtCl_4$ , C = 7.2; H = 2.4; N = 5.6; Pt = 40.2 per cent.

The undried salt contained  $H_2O = 3.8$ . Calculated  $1H_2O = 3.6$  per cent.; also 39.1 per cent. Pt; calculated, Pt = 39.0 per cent.

This curious platinum salt was, therefore, evidently the salt of propenediamine,  $\begin{array}{c} CH_3 \cdot C \cdot NH_2 \\ | \\ HC \cdot NH_2 \end{array}, H_2PtCl_6$ , and this diamine had been produced by the decomposition of the amidolutidone,



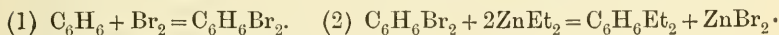
But it is remarkable that such a change should occur, especially as lutidone itself is such a stable pyridine compound, and is not liable to be reconverted into open chain compounds. An attempt was made, but without success, to prepare the free base, propenediamine, from

the platinum salt by precipitating the platinum with sulphuretted hydrogen and subsequently evaporating; the residue of the hydrochloride was excessively soluble in water, and when treated with soda gave some ammonia gas, and the solution at once reduced silver nitrate solution, but owing to the small quantity of the platinum salt at our disposal, we were unable to isolate the free base.

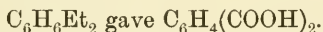
### XIX.—*Note on the Action of Bromine on Benzene.*

By J. NORMAN COLLIE, Ph.D., F.R.S., and COLIN C. FRYE, Pharmaceutical Society of Great Britain, Bloomsbury Square.

IN a former paper communicated to the Society (Trans., 1897, 71, 1013), one of the authors referred to a paper by Ador and Rilliet (*Ber.*, 1875, 8, 1286), where it was stated that, by the action of a small quantity of bromine on excess of benzene, bromine additive products are formed, which, on treatment with zinc ethide and subsequent oxidation yield metabromophthalic acid and metaphthalic acid. The reaction was supposed to take place according to the following equations.



And on oxidation with chromic acid



Besides the two meta-acids mentioned above, they also obtained benzoic acid, parabromobenzoic acid, and terephthalic acid, but no phthalic or orthobromobenzoic acids.

This formation of meta-compounds by direct addition of bromine to benzene is one of great interest, and the fact that no ortho-disubstitution derivatives seemed to be produced rendered it still more perplexing.

We have repeated the work of Ador and Rilliet, and find it to be substantially correct, but as we have been able to prove that ortho-di-derivatives are also produced, and that a different result is obtained when bromine and benzene are allowed to react in the dark or in sunshine, we have thought it worth while to record the facts.

The method employed by Ador and Rilliet was briefly the following. Dry benzene (200 grams) was mixed with bromine (6 grams), the mixture exposed to sunlight, the product washed with water and a little dilute soda, dried, and boiled with zinc ethide for 20 hours. The excess of benzene was then distilled off, and all that boiled above  $110^\circ$  was collected and oxidised with chromic acid.

Our experiments were made on a somewhat larger scale, in the hopes of obtaining perhaps enough of the ethyl compounds to separate by



fractional distillation, but this was found to be impossible, as only very small quantities of the substances were produced, and the product consisted of a mixture having no definite boiling point.

Our first series of experiments consisted in allowing the dry benzene (which had been carefully prepared from pure crystalline benzene by distillation) and bromine (also purified) to remain in the dark for 24 hours. From 500 grams of benzene and 50 grams of bromine we obtained only about 7 c.c. of liquid boiling above  $100^{\circ}$ . In another experiment with the same amounts, we obtained somewhat more, but the reaction did not seem to have proceeded far, and much bromine remained unacted on. The 7 c.c. of liquid boiled between  $100^{\circ}$  and  $270^{\circ}$ , and at no point were we able to say more passed over than at any other.

The various fractions collected at  $100-120^{\circ}$ ,  $120-170^{\circ}$ ,  $170-210^{\circ}$ , and above  $210^{\circ}$  were separately oxidised with potassium permanganate.

The two fractions of lower boiling point gave considerable quantities of benzoic acid (m. p.  $120^{\circ}$ ), but mixed with it were traces of a bromorthophthalic acid, as eosin was formed when it was heated with resorcinol and sulphuric acid. From the fraction  $170-210^{\circ}$ , we were able to isolate an acid containing bromine which melted at  $248^{\circ}$ ; parabromobenzoic acid melts at  $251^{\circ}$ . A determination of bromine gave 39.0 per cent.;  $\text{C}_6\text{H}_4\text{Br}\cdot\text{COOH}$  requires  $\text{Br} = 39.8$  per cent.; the amount of silver in the silver salt was also determined, Found  $\text{Ag} = 37.6$ ;  $\text{C}_6\text{H}_4\text{Br}\cdot\text{COOAg}$  requires  $\text{Ag} = 35.6$  per cent. The amount of acid at our disposal, however, was so exceedingly small (about 0.3 gram) that we were unable to purify it properly, which fact may account for the excess of silver found in the analysis of the salt. From the fraction  $210^{\circ}$  and above, a very small amount of acid was obtained which was partly soluble in hot water; it did not give any reaction for an orthodicarboxylic acid of benzene when heated with resorcinol and sulphuric acid, it melted at  $185^{\circ}$ , and sublimed at a higher temperature. An analysis gave 39.8 per cent. of bromine, but its melting point does not agree with that of any of the bromobenzoic acids.

Our next experiments were made with the same quantities of benzene and bromine, which were carefully purified, dried, and mixed at  $-10^{\circ}$ ; the mixture, after being exposed to sunlight for 6 hours, was washed with water, dried over calcium chloride, and 40 grams of zinc ethide were then distilled into the dry mixture and the whole boiled for 24 hours (3 days). The product was washed with dilute hydrochloric acid, dried, and fractionated; 34 c.c. passed over above  $100^{\circ}$ , this was separated into the following fractions,  $100-120^{\circ}$  about 5 c.c.,  $120-150^{\circ}$  about 4 c.c.,  $150-200^{\circ}$  about 5 c.c., above  $200^{\circ}$  about 20 c.c. These fractions were oxidised, as in the preceding case, with potassium permanganate. The first fraction gave large quan-

tities of benzoic acid, but after evaporating the benzoic acid on the water bath, a residue was left which gave a strong fluorescein reaction with resorcinol and sulphuric acid, proving the presence of an ortho-phthalic acid. The second fraction gave also chiefly benzoic acid, but after this acid had been volatilised at  $100^{\circ}$ , there remained a small amount of an acid which was almost insoluble in cold water; it was soluble in ether and slightly so in hot water, and was purified by several times dissolving it in alcohol and precipitating with water. It did not contain bromine, and gave no phthalic acid reaction with resorcinol. On comparing it with isophthalic acid, it seemed identical under the microscope, both when crystallised from water and when sublimed. When the two acids were heated, they both behaved in a similar manner, melting and subliming at about  $310^{\circ}$ .

Some of the salts of this acid were compared with those of isophthalic acid; with silver nitrate it gave a white precipitate, with barium chloride a white precipitate, and with ferric chloride a reddish-brown precipitate, identical with corresponding precipitates obtained with isophthalic acid. Its silver salt gave  $\text{Ag} = 57.6$  per cent.,  $\text{C}_6\text{H}_4(\text{COOAg})_2$  requiring  $\text{Ag} = 56.8$  per cent. As the only other acid that it could have been was terephthalic, pure terephthalic acid was also compared with it under the microscope, but the two appeared quite different in crystalline form. It seems certain, therefore, that Ador and Rilliet's observation was correct, and that when bromine is allowed to react with benzene in sunlight, meta-di-derivatives are formed. The only acid that could be separated from the fraction of highest boiling point was parabromobenzoic acid melting at  $250^{\circ}$ .

It appears, therefore, from these results, that when bromine is allowed to act on benzene in sunlight some dibrom-additive products are formed in very small quantities, which by the reactions employed can be converted into dicarboxylic acids of benzene; as we have obtained acids that yield fluorescein and eosin (when heated with resorcinol), parabromobenzoic acid and metaphthalic acid, it follows that bromine is capable of reacting with benzene to form ortho-, meta-, and para-compounds. The explanation of this is difficult, and seems entirely at variance with the action of bromine on bromobenzene.

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## XX.—Benzene Hexabromide.

By FRANCIS EDWARD MATTHEWS, Ph.D.

IN the course of work on the halogen hexa-additive compounds of benzene and its derivatives, the author has had occasion to prepare the hexabromide of benzene in considerable quantity.

As benzene hexachloride exists in two isomeric forms, the existence of two modifications of the hexabromide was to be expected, but, although carefully looked for, no indication of the second modification was obtained.

As the hexabromide prepared by the method described in a former paper (*Trans.*, 1892, **61**, p. 110) seemed homogeneous, its further investigation was abandoned until a paper was published by Orndorf and Howells (*Amer. Chem. J.*, 1896, **18**, pp. 312—319), who succeeded in isolating a very small quantity of a second modification from the hexabromide prepared by the method suggested in my paper, but not from that prepared by other methods.

Having a considerable amount of crude material on hand, I once more attempted to obtain the second modification, but in the course of a series of fractional extractions with chloroform performed on some half-pound of substance, I could find no evidence of the more insoluble modification, as the crystals obtained from the final extract had the same crystalline form, melting point, and solubility as those from earlier portions.

In the method of preparation adopted by Orndorf and Howells there was, however, one slight difference from that which I used, and this may account for the difference in the result. After exposure to sunlight, they evaporated the mixture of bromine, water, and benzene to dryness, and subsequently made extracts of the residue; my crude material consisted solely of the solid precipitated during the action of sunlight, which was roughly freed from the mother liquor by filtration through coarse muslin, and by subsequent washing with benzene, so that it seems probable that the second modification, although very insoluble, is produced in such small quantity as not to precipitate spontaneously from the mother liquor, which consists of benzene, a considerable quantity of bromobenzene, and a small amount of paradibromobenzene.

Bromobenzene does not appear to be capable of forming a hexabromide under the conditions in which benzene hexabromide is produced, the bromine displaces hydrogen in the nucleus, and paradibromobenzene is almost exclusively formed.

Bromobenzene also could not be made to form a hexachloride; on mixing bromobenzene with water and passing in chlorine, bromine is liberated, rapidly in sunlight, more slowly in diffused daylight, and on continuing the action a complex mixture of halogen compounds is formed.

In all its reactions save one, benzene hexabromide behaves as has been described by previous investigators; the sole difference is the action of alcoholic alkali hydroxides on it. According to previous work, benzene hexabromide is decomposed by alcoholic solutions of

alkalis, similarly to the hexachloride, quantitatively into 1:2:4 tri bromobenzene with the removal of 3 mols. HBr. This I have found not to be the case, as on boiling the pure recrystallised hexabromide with alcoholic soda, more bromine is removed than is required by the equation



Some pure benzene hexabromide, recrystallised from chloroform, and which gave on analysis 85.44 per cent. of bromine (Theory 86.02) was decomposed with excess of alcoholic soda free from chlorine, and the amount of bromine in solution was determined.

0.2298 gram  $\text{C}_6\text{H}_6\text{Br}_6$  gave 0.2707 gram AgBr. Br = 50.1.

0.2154 „  $\text{C}_6\text{H}_6\text{Br}_6$  „ 0.2444 „ AgBr. Br = 48.3.

Theory for removal of  $\text{Br}_3 = 43.0$ , of  $\text{Br}_4 = 57.3$  per cent.

From the above it follows that 1 mol.  $\text{C}_6\text{H}_6\text{Br}_6$  parts with about  $3\frac{1}{2}$  atoms of bromine to alcoholic soda, and, in order to identify the products, the reaction was carried out on a much larger scale. After the hexabromide had been boiled with excess of alcoholic soda for some time and everything had gone into solution, excess of water was added, and the semi-solid precipitate extracted with ether; the solution was dried, the ether distilled off, and the residue fractionally distilled, when the whole came over between  $210^\circ$  and  $280^\circ$ , two principal fractions being obtained, the first distilling at  $220$ — $230^\circ$ , and the other at  $260$ — $270^\circ$ . Both of these portions solidified on standing, and the fraction  $260$ — $270^\circ$ , after recrystallisation from benzene, gave the following figures on analysis.

0.2820 gave 0.5070 AgBr. Br = 76.5.  $\text{C}_6\text{H}_3\text{Br}_3$  requires Br = 76.2 per ct.

It was identified as unsymmetrical tribromobenzene from the above figures by its boiling point and melting point ( $43^\circ$ ). The other chief fraction,  $220$ — $230^\circ$ , was freed from oily matter on a porous plate and recrystallised from benzene, in which it was very soluble, by spontaneous evaporation. It was then found to melt at  $86$ — $87^\circ$ , and gave the following figures on analysis.

0.1936 gave 0.3094 AgBr. Br = 68.0.

0.2744 „ 0.3096  $\text{CO}_2$  and 0.0490  $\text{H}_2\text{O}$ . C = 30.8; H = 2.0.

0.1032 „ 0.1160  $\text{CO}_2$  „ 0.0180  $\text{H}_2\text{O}$ . C = 30.6; H = 1.9.

$\text{C}_6\text{H}_4\text{Br}_2$  requires Br = 67.8; C = 30.5; H = 1.7 per cent.

The substance is therefore a dibromobenzene, and from its melting point and from the melting point of its nitro-derivative ( $83^\circ$ ) it appears to be the para-compound. Between  $230^\circ$  and  $260^\circ$ , small fractions of liquid substances were obtained, but as the small amount precluded their separation by fractional distillation, an attempt was made to



separate them by fractional crystallisation of their nitro-derivatives; the presence of orthodibromobenzene was suspected, but the results obtained did not completely substantiate its presence.

Tribromobenzene yields no trace of dibromobenzene, neither does it part with bromine when acted on by boiling alcoholic soda; the formation of the dibromobenzene, therefore, takes place during the decomposition of the benzene hexabromide.

Benzene hexabromide, on reduction with nascent hydrogen in acid alcoholic solution, yields benzene. The benzene thus obtained was found to yield both modifications of benzene hexachloride on treatment with chlorine.

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## XXI.—*Observations on the Influence of the Silent Discharge on Atmospheric Air.*

By WILLIAM ASHWELL SHENSTONE and WILLIAM T. EVANS.

NEARLY forty years ago, the late Professor Andrews observed that when air is exposed to the action of the silent discharge of electricity it contracts to a certain extent, that if it be then left in contact with oil of vitriol for a few hours it undergoes further contraction,\* and that if the residue be afterwards again submitted to the discharge its volume may be yet further diminished. He accounted for these phenomena by supposing that one or more of the higher oxides of nitrogen had been formed from the air. At the same time, Andrews called attention to the fact that it is impossible to generate ozone in oxygen which contains small quantities of nitrogen if the mixture has recently been exposed to the action of disruptive discharge. This he also attributed to the "presence of a trace of hyponitric acid gas produced by the electrical sparks" (*Trans. Roy. Soc.*, 1860, p. 127).

Berthelot (*Compt. rend.*, 1881, 92, 82), and Hautefeuille and Chappuis (*Compt. rend.*, 1881, 92, 80 and 134) have also recognised oxides of nitrogen among the products of the action of the silent discharge on atmospheric air, and most of Andrews' successors in this field of work have taken pains to employ very carefully purified oxygen for their experiments. Our knowledge, however, of the phenomena described by Andrews still stands almost at the stage at which he left it; and, therefore, as the subject is both interesting from the scientific point

\* The oil of vitriol is not mentioned in Andrews' description of his experiment, but it was present in the manometers he used.



of view, and of some importance to those who seek to apply ozone medically, and for other technical purposes, we have recently spent some time in an attempt to follow up this part of Andrews' beautiful researches.

We are conscious that the work described in this paper by no means exhausts our subject, but we venture to present the results already obtained to the Society at this stage, since we hope they may be found interesting and useful to other workers, and because the difficult character of the experiments still before us may make our future progress rather slow.

### *I. A Method of Detecting Nitric Peroxide in the Presence of Ozone.*

The oxide of nitrogen produced by the action of the silent discharge on air always exists in the presence of excess of oxygen or ozone; therefore, as there is no reason to suspect that nitrous oxide is formed by the discharge, nitric peroxide is the only oxide of nitrogen which is at all likely to be met with; in order to detect and estimate this in the presence of ozone, we draw the gas to be tested through a very dilute solution of soda, and then determine the nitrite formed by means of Riegler's reagent (Abstr., 1897, ii, 464). As the action of the latter seems to depend in the first instance on the forming of  $\alpha$ -diazonaphthylsulphonic acid, by the interaction of nitrous acid with 1:4-naphthylaminesulphonic acid, and on its subsequent conversion into a red dye, its usefulness, as might be expected, is not affected by the presence of ozone, and we believe it to be very suitable for the purpose to which we have applied it.

### *II. Influence of the Silent Discharge on Moist Air.*

*Experiment I.*—An ozone generator provided with a manometer (Trans., 1893, 63, p. 943, Fig. 3) was filled with atmospheric air saturated with water at  $0^{\circ}$ , from which the ammonia and carbon dioxide had previously been removed; the contents of the apparatus were then submitted to the discharge at  $0^{\circ}$ , as described in previous accounts of similar experiments on oxygen (*loc. cit.*, p. 938). The difference of potential employed corresponded to 44.4 C. G. S. units (electrostatic), and great care was taken not to raise the temperature of the gas by employing too rapid a succession of discharges. As soon as the discharge was applied to the air, it condensed rapidly and to a remarkable extent, presently the rate at which it contracted became slower, and then, suddenly, it commenced to re-expand; the latter change ceased whenever the discharge was discontinued, but occurred again as often as the sparking was recommenced. When a large part of the ozone formed during the first stage had evidently been

destroyed, but while a little still remained, a hole was pierced in the bottom of the ozone generator, another at the end, *Z* (*loc. cit.*), of the manometer, and its contents were drawn through cold water, which was afterwards examined for nitrites in the manner described above. Unmistakable indications of the presence of nitric peroxide were obtained.

Owing to the suddenness with which the secondary action of the discharge set in, we are unable to state exactly the maximum amount of ozone formed. We satisfied ourselves, however, from the measurements taken, that not less than 91 per cent. of the oxygen present had been converted into ozone; we believe this proportion has never been exceeded except in one of our own experiments.\*

Having now obtained a general idea of the mode of action of the silent discharge on air, we arranged our subsequent experiments largely for the purpose of gaining answers to the following questions.

*a.* What is the highest yield of ozone that can be obtained from air under the most favourable conditions?

*b.* At what stage is nitric peroxide first formed, and what is its subsequent history?

*c.* What influence has the presence of moisture on the various phenomena under investigation?

In all the experiments described in this paper, we employed the ozone generator formerly used by one of us for examining the influence of the silent discharge on moist, and on carefully dried oxygen. The present work on air is therefore strictly comparable with the former work on oxygen (*Trans.*, 1897, **71**, p. 471). A small tail was added to the bottom of the ozone generator (*loc. cit.*, Fig. 3), in order that we might attach an absorption tube to it by a paraffin joint when it was necessary to withdraw its contents in order to test for nitric peroxide.

### III. *The Maximum Yield of Ozone produced by the Action of the Silent Discharge on Air at 0°.*

From the results of a number of experiments, we found that, in order to produce the largest proportion of ozone from air, it is necessary that moist air should be employed, also that great care be taken not to apply the discharges in too rapid succession, and that frequent intervals be allowed for cooling towards the end of the operation.

It is rather difficult to hit the point at which the condensation of

\* Brodie (*Trans. Roy. Soc.*, 1874, **164**, p. 101) submitted carbon dioxide to the action of the silent discharge and found that as much as 85 per cent. of the oxygen liberated might consist of ozone. Only a few c.c. of ozone were obtained, however, from a considerable volume of carbon dioxide in Brodie's experiment.

the air attains its maximum, because immediately this point is reached the contents of the ozoniser re-expand rapidly. Ozonised air, moreover, appears to be far more sensitive to rise of temperature, such as may be caused by the use of a too rapid succession of discharges, than is the case with ozonised oxygen. The effect of this sensitiveness is well illustrated by the results of our three earliest experiments.

*Experiment I.*—This was the preliminary experiment described above. The discharges were delivered at a moderate rate with frequent intervals for cooling, air saturated with water at 0° being used.

91 per cent. of the oxygen present was converted into ozone.

*Experiment II.*—Air saturated with water at 0° was used, the succession of discharges was more rapid, but the intervals for cooling were the same as in the previous experiment.

Only 82.1 per cent. of the oxygen was converted into ozone.

*Experiment III.*—The dynamo did not work well during this experiment, and consequently the succession of discharges was *very* slow; moist air was used, and the intervals for cooling were the same as in the other two experiments.

98 per cent. of the oxygen present was converted into ozone.

If the last of these results be compared with what has previously been done, it will be seen that not only does the proportion of the oxygen which was ozonised far exceed anything previously obtained, but also that the charge of ozone carried by the gas is exceedingly high, much higher, for example, than was obtained by one of us, by means of the same ozone generator, and under the most favourable conditions from moist oxygen, namely, 13.6 per cent. (*Trans.*, 1897, 71, p. 475).

#### IV. *Experiments to ascertain the Influence of Moisture on the Formation of Ozone from Air.*

It has been shown by one of us, in a previous paper, that well-dried oxygen yields little or no ozone when it is subjected to the action of the silent discharge (*Trans.*, 1897, 71, p. 479); a single experiment such as was then performed occupied many months, and during its progress the ozone generator was not available for other work. To avoid such cause of delay on this occasion, we dried our air in a more simple manner, partly because it seemed almost a foregone conclusion that very highly-dried air would, like oxygen, be practically unaffected by the discharge, and partly because the progress of the research as a whole was more important at the time than the making of a single experiment to minutely investigate one particular point.

Before we made the experiments with dried air, the ozone generator was dried by heating it, when exhausted, with the little furnace previously described (*loc. cit.*, 478); it was then filled with dried air

re-exhausted and re-filled. The air was dried by passing it slowly over a column of purified phosphoric anhydride (Trans., 1893, 63, p. 475) which had previously been freed from carbon dioxide.

It should be mentioned that the air used in VI was more nearly dry than that used in IV and V, as it was purposely passed at a slower rate over the drying material.

A.—Results obtained with wet oxygen.

Experiment I.	91	per cent. of the oxygen present was ozonised.
Experiment II.	82·1	” ” ”
Experiment III.	98	” ” ”

B.—Results with dried oxygen.

Experiment IV.	66·7	per cent. of the oxygen present was ozonised.
Experiment V.	67·0	” ” ”
Experiment VI.	60·0	” ” ”

Similar results were obtained in the course of two other experiments with moist and dried air ; in these, the air was rapidly ozonised for the purpose of examining its composition at later stages, and consequently the maximum proportion of oxygen ozonised was smaller than before, but the results tell the same tale.

A.—Dried air 63·5 per cent. of the oxygen was ozonised.

B.—Moist air 80·0 ” ”

#### V. *Experiments to Trace the Formation of Nitric Peroxide from Air by means of the Silent Discharge.*

We have seen from Experiment I that air which has been highly charged with ozone, and subsequently partly reduced by the continued action of the silent discharge, contains nitric peroxide. In order to trace the formation of the latter substance at various stages of an experiment and, if possible, to learn in what manner its appearance is connected with the destruction of the ozone which follows the continued application of the discharge, we made the following experiments.

*Experiment VII.*—The ozone generator was filled with dried air, and its contents submitted to the action of the silent discharge until the rate at which the gas contracted and the proportion of oxygen ozonised, 63·5 per cent., indicated that the point of maximum contraction was nearly reached ; the contents of the ozone generator were then drawn off and examined for nitric peroxide.

No nitric peroxide was found.

*Experiment VIII.*—This was a repetition of the previous experiment, except that the action of the discharge was not carried quite so far, only 61·8 per cent. of the oxygen being ozonised. In this case, also,



no nitric peroxide could be detected, although so small a quantity as 0.000001 gram of nitrous anhydride can be recognised by Riegler's reagent in 100 c.c. of water.

*Experiment IX.*—The ozone generator having been recharged with dried air, its contents were submitted to the silent discharge until a portion of the ozone first formed, 67 per cent., was again destroyed. The residue was then tested for nitric peroxide.

No less than 0.041 c.c. was found.\*

The observed increase of the volume of the gas in this experiment corresponded to a reduction of the percentage of oxygen ozonised from the maximum 67 to 54 per cent.; the actual proportion of ozone remaining was, however, somewhat less than 54 per cent., because some nitric peroxide had been simultaneously formed.

Similar experiments were next made upon moist air.

*Experiment X.*—Moist air was submitted to the discharge until 80 per cent. of its oxygen was ozonised; as the rate at which it contracted had then become slow, the discharge was stopped and the contents of the apparatus were tested as before.

No nitric peroxide was detected.

*Experiment XI.*—This experiment was a repetition of X, and gave a similar result.

*Experiment XII.*—Moist air was submitted to the discharge until some of the ozone first formed had been destroyed again, but the destruction of the ozone was not carried so far as in the corresponding experiment with dried air.

The residue was found to contain 0.020 c.c. of nitric peroxide,  $\text{N}_2\text{O}_4$ .\*

The expansion at the second stage corresponded in this case to a reduction of the ozone from the maximum 82.1 to 72 per cent., but allowance must be made for the nitric peroxide simultaneously formed.

From these results, it is evident that nitric peroxide is not produced by the action of the silent discharge on air, either moist or when dried, at  $0^\circ$ , until a large proportion of the oxygen present has been converted into ozone; and this fact, together with the rapid destruction of ozone which accompanies the appearance of the nitric peroxide, suggests the idea that the latter may be formed at the expense of the

\* These volumes are calculated on the assumption that the formula of nitric peroxide is  $\text{N}_2\text{O}_4$ . There is reason to believe, however, that, under the conditions of the experiment, this gas is partly dissociated.

It is of course possible that the presence of ozone with the moisture, and nitric peroxide, &c., may favour the formation of nitric acid when the mixed gases are drawn through a dilute alkaline solution, and thus lead one to underestimate the amount of nitric peroxide present. This, however, if true, would rather increase the significance of the results obtained in experiments IX and XII, and these alone are likely to have been affected by such a disturbing cause.



ozone, and not by the combining of nitrogen and ordinary oxygen. This view of the matter is supported by the result of Experiment III (p. 249), which shows that only a few tenths of a per cent. of oxygen were present in the gas at the moment when the formation of the nitric peroxide probably began, and is further upheld by the important fact that the formation of nitric peroxide from air under the influence of the silent discharge is distinctly retarded by the presence of water vapour and promoted by dryness. (Compare IX with X and XI. Compare also the results of I, II and III, in which 82 to 98 per cent. of oxygen was probably ozonised before sensible quantities of nitric peroxide were formed, with those of IV, V, VI, in which only 60—67 per cent. of oxygen was ozonised when its destruction, presumably due to nitric peroxide, set in.) For it has previously been shown by one of us (Trans., 1897, 71, *loc. cit.*) that the stability of ozone is increased by the presence of moisture, which might lead us to expect its power as an oxidising agent to be lower in the presence of water than when dry. Ordinary oxygen, on the other hand, is well known to oxidise best in many cases in the presence of water.

But whatever may be the truth in regard to this matter, it is at any rate very interesting to meet with a fresh case of chemical change which is retarded by the presence of water vapour (see also Trans., 1897, 71, *loc. cit.*).

In connection with the above, it must be remembered that although the presence of a large proportion of ozone is necessary for the formation of nitric peroxide from air by the influence of the silent discharge at 0°, yet a rapid destruction of ozone sets in simultaneously, or almost simultaneously, with the formation of nitric peroxide. The latter change is accompanied by the destruction of a great part of the nitric peroxide first formed.

The following examples will make this clear.

A. In Experiment IX, some dry air was ozonised, then a part of the ozone was destroyed; the residual contents of the ozoniser were found to contain 0·041 c.c. of nitric peroxide.

B. Some moist air was similarly treated (Experiment XII); it yielded 0·020 c.c. of peroxide,  $\text{N}_2\text{O}_4$ .\*

C. Some dry air was ozonised and then re-sparked until the final volume showed that all but a trace of the ozone was destroyed; it afterwards yielded only 0·007 c.c. of peroxide,  $\text{N}_2\text{O}_4$ .

D. Another specimen of dry air was similarly treated; it yielded 0·006 c.c. of peroxide,  $\text{N}_2\text{O}_4$ .

E. Some moist air was ozonised and then submitted to the continued

\* The difference in the hygrometric state of the air may possibly account for the difference between the results of A and B, since the presence of moisture retards the formation of nitric peroxide.

action of the discharge until only a trace of ozone remained; it was found to contain only 0.008 c.c. of peroxide,  $N_2O_4$ . These last three results do not, it is true, agree very closely, but the difference between the proportions of nitric peroxide present in A and B, when most of the ozone still remained undestroyed, and that found in C, D, and E, after the ozone was destroyed, are sufficiently marked.

On the other hand, ozone and nitric oxide do not thus destroy each other at  $0^\circ$ , except under the influence of the silent discharge, if moist. For example, on one occasion, 8.405 c.c. of moist gas containing 0.824 c.c. of ozone and 0.020 of nitric peroxide, or an equivalent volume of the products of its dissociation, were preserved for more than half an hour without any sensible change of volume taking place, and other similar observations have been made. We have reason to suspect, however, that above  $0^\circ$ , or if dry, these gases interact far more readily. Experiments on this subject are being carried out.

Finally, our experience entirely confirms the statement made by Andrews, that oxygen cannot be converted into ozone if a trace of nitric peroxide be present. In one experiment made to test this point, 8.74 c.c. (at 760 mm. and  $0^\circ$ ) of dried air was ozonised, and the product, 8.35 c.c., was then submitted to the continued action of the discharge until it ceased to expand; its volume was then 8.72 c.c. After this it was submitted to the silent discharge for 75 minutes, but it remained quite unaffected, and at the end its volume was still 8.72 c.c.

### *Summary.*

1. Oxygen, diluted by nitrogen, yields a higher proportion of ozone when submitted to the influence of the silent discharge, under given conditions, than pure oxygen; the proportion of oxygen ozonised may be as high as 98 per cent. of the oxygen submitted to the discharge. This fact deserves the notice of those who are interested in the technical applications of ozone.

2. If the process of ozonising air be not pressed too far, no peroxide of nitrogen will make its appearance.

3. The presence of water vapour is very favourable to the production of a high yield of ozone, and retards the appearance of nitric peroxide.

4. At a certain stage in the process of ozonising the oxygen of the air, which depends on the amount of vapour present, and probably also on the temperature of the gas, nitric peroxide is formed. Its appearance is immediately, or almost immediately, followed by a rapid disappearance of the ozone, and this in its turn results in the destruction of most of the nitric peroxide.

5. That, as stated by Andrews, the presence of a trace of nitric per

oxide renders it impossible to convert oxygen into ozone by means of the silent discharge.

6. That nitric peroxide and ozone when moist do not mutually destroy one another at  $0^{\circ}$ , or do so at a very slow rate, unless they are under the influence of the silent discharge.

CLIFTON COLLEGE.

February, 1898.

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## XXII.—*Preparation and Properties of Orthochlorobromobenzene.*

By JAMES J. DOBBIE, M.A., D.Sc., and FRED. MARSDEN, M.Sc., Ph.D.

IN the course of an investigation on the halogen derivatives of benzene, we have had occasion to prepare in quantity all the modifications of its di-derivatives containing chlorine and bromine.

We find that orthochlorobromobenzene has not hitherto been described, and the object of the present communication is merely to place its properties on record. The starting point of its preparation was orthonitrobromobenzene; this was made by nitrating bromobenzene in the cold in the manner described by Coste and Parry (*Ber.*, 1896, 29, i, 788); this gave very satisfactory results, but we found it most convenient to separate the ortho- and para-compounds by grinding them up in a mortar with small quantities of cold methylated spirits and filtering, repeating the operation until the filtrate became colourless. The orthonitrobromobenzene dissolved, and after the solvent had evaporated was obtained in long needles which melted at  $42^{\circ}$  after recrystallisation.

On reducing the orthonitrobromobenzene to the corresponding bromaniline, Hübner and Alsberg (*Annalen*, 1870, 156, 316), and later Fittig and Mager (*Ber.*, 1874, 7, 1179), found great difficulty in obtaining the latter in the solid state; we experienced the same difficulty, which was completely overcome, however, when we added the nitrobromobenzene in alcoholic solution, instead of in the solid state, to the slightly warmed reducing mixture of stannous chloride and hydrochloric acid. On shaking vigorously, the reduction proceeded with development of heat, and after cooling, adding excess of caustic soda and distilling with steam, the oil which came over solidified in the receiver; after recrystallising, it melted at  $32^{\circ}$ .

To convert the orthobromaniline into orthobromochlorobenzene, it was diazotised in the usual manner, and the solution of the diazo-compound added to a warm solution of cuprous chloride. The oil which separated was then distilled over with steam, the distillate

extracted with ether, the extract dried over calcium chloride, and after driving off the ether the residue was fractionally distilled. The greater part came over between  $200^{\circ}$  and  $202^{\circ}$ .

The halogens were determined by Carius' method.

0.302 gave 0.5168 mixed silver haloids.  $\text{AgBr} = 0.2948$ ;  $\text{AgCl} = 0.222$ .

Br = 41.52 per cent.	} Found	41.77	}	Calculated.
Cl = 18.18 per cent.				

Orthochlorobromobenzene is a clear, straw-coloured liquid having a strong aromatic odour. It boils constantly at  $204^{\circ}$  (mercury column in vapour, pressure 765 mm.), and does not solidify at  $-10^{\circ}$ . Its sp. gr. = 1.6555 at  $12.5^{\circ}$ , and  $\mu_D = 1.583$  at  $15^{\circ}$ .

For purposes of comparison, we determined the sp. gr. and refractive index of metachlorobromobenzene and found its sp. gr. = 1.6274 at  $14^{\circ}$ , and  $\mu_D = 1.578$  at  $15^{\circ}$ .

The following table gives some of the constants of the chlorine and bromine di-derivatives of benzene.

	Boiling points.			Sp. gr.		
	Ortho.	Meta.	Para.	Ortho.	Meta.	Para.
$\text{C}_6\text{H}_4\text{Br}_2$ .....	$223.8^{\circ}$	$219.4^{\circ}$	$219^{\circ}$	1.977	1.955	—
$\text{C}_6\text{H}_4\text{ClBr}$ .....	204	196	$196.3$	1.6555	1.6274	
$\text{C}_6\text{H}_4\text{Cl}_2$ .....	179	172	172	1.3254	1.307	

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### XXIII.—*Preparation of Dry Hydrogen Cyanide and Carbon Monoxide.*

By JOHN WADE, B.Sc. and LAURENCE C. PANTING, M.B., B.Ch.

It is obvious that, by the action of sulphuric acid on potassium cyanide, both hydrogen cyanide and carbon monoxide may be formed, but it does not seem to be generally known that by suitably varying the concentration of the acid, a practically quantitative yield of either product can be obtained.

The alkali cyanide is of course decomposed by sulphuric acid of all concentrations, and on distillation with the dilute acid yields dilute hydrocyanic acid; with a less dilute acid, however, less water passes over, and with a mixture of equal volumes of sulphuric acid and water, the hydrogen cyanide contains only such small quantities of aqueous



vapour as are readily removed by passing it over warm calcium chloride.

When a larger proportion of sulphuric acid is used, a certain amount of carbon monoxide is formed, and as the concentration of the acid is increased the volume of gas increases, whilst the amount of hydrogen cyanide diminishes; and finally, when ordinary concentrated sulphuric acid is allowed to act on the cyanide, nearly pure carbon monoxide is evolved in almost theoretical quantity.

#### *Preparation of Dry Hydrogen Cyanide.*

In preparing hydrogen cyanide free from water, ordinary 98 per cent. lump cyanide (100 grams), in pieces of the size of a hazel nut, is placed in a capacious flask, provided with a drop-funnel and delivery tube, the latter being connected through two U-tubes of calcium chloride with a series of two Y-tubes (U-tubes furnished with tubuluses), the stems of which pass through the necks of inverted bell-jars into two receiving bottles. The drying tubes are immersed in a vessel of water at about  $35^{\circ}$ , and are filled respectively with pieces of fused calcium chloride and fragments of the well-dried porous material. The condensing tubes are cooled, the first with ice and water, and enough salt to reduce the temperature to about  $-10^{\circ}$ , the second with ice and salt at about  $-20^{\circ}$ ; it is not advisable to cool the first tube much below the temperature specified, or the tubulus may become choked with crystals of the frozen acid. The receiving bottles are cooled with ice, and closed with corks through which the tubuluses pass. The great bulk of the acid collects in the first receiver, only 2 or 3 per cent. passing on to the second, and practically none escapes condensation.

A current of air having been blown through the drying and condensing tubes, to dry the latter, and the cooling and warming baths brought to the requisite temperatures, a cold mixture of equal volumes of sulphuric acid and water (100 c.c. of each) is allowed to drop on to the cyanide at such a rate that about one drop of hydrogen cyanide falls into the first receiver per second. As each drop of acid reaches the cyanide, there is a brisk effervescence and frothing, with development of heat, the mixture becoming sufficiently hot to retain the potassium hydrogen sulphate in solution. At the end of the action, the vapour in the flask and solution is expelled by heating the latter to incipient ebullition.

In this way, with the quantities specified, about 40 grams (58 c.c.) of practically pure hydrogen cyanide is obtained, which on rectification from a little phosphorus pentoxide over a bath of warm water, passes over entirely between  $26.2^{\circ}$  and  $26.3^{\circ}$ . The average yield of the pure



substance is 38·5 grams, the calculated amount being 40·8 grams ; the maximum yield obtainable from 100 grams of potassium ferrocyanide is 15·3 grams.

*Preparation of Carbon Monoxide.*

In preparing carbon monoxide from potassium cyanide, the same generating apparatus is used, cold concentrated sulphuric acid being substituted for the diluted acid. The gas is purified from accompanying hydrogen cyanide vapour, and in certain eventualities from carbon and sulphur dioxides, by washing twice with strong potash solution ; as a rule, it is quite free from carbon dioxide, but commercial lump cyanide sometimes contains a little carbonate.

If the acid is allowed to flow too fast on to the cyanide, so that the temperature becomes unduly high, the sulphuric acid is reduced, and sulphur and carbon dioxides are formed ; but this does not occur if the action is kept within moderate bounds. Even with a slow delivery of the acid, the evolution of the gas is very rapid, and several litres may be prepared in a few minutes.

The yield of pure carbon monoxide, completely soluble in cuprous chloride solution, obtained in this way from 50 grams of cyanide, varies from 14 to 16 litres, the calculated quantity at 15° and 760 mm. being 17·4 litres, moreover, the process is quite as convenient as the formic acid process, and much more economical.

The action of concentrated sulphuric acid on anhydrous hydrogen cyanide is similar. The mixture soon becomes hot, but although some of the cyanide is of course volatilised, the greater part enters into combination, and on applying heat abundance of carbon monoxide is evolved. If the liquid is overheated, or even in the cold, if sufficient time is allowed, carbon and sulphur dioxides are formed, as with the alkali cyanide.

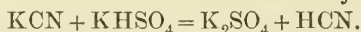
*The Mechanism of the Carbon Monoxide Reaction.*

It would appear at first sight that the quantitative conversion of the carbon of potassium cyanide into carbon monoxide is effected by ordinary hydrolysis and dehydration, the hydrogen cyanide being converted into formic acid, and this into carbon monoxide. Whether hydrogen cyanide be formonitrile,  $\text{H}\cdot\text{C}:\text{N}$ , or what may be termed carbamine,  $\text{H}\cdot\text{N}:\text{C}$ , the same products of hydrolysis will be formed : from the nitrile a carboxylic acid (formic acid) and ammonia, and from the carbamine, an amine (ammonia) and formic acid. Sufficient water for the purpose is indeed present in ordinary concentrated sulphuric acid, assuming the complete action to be represented by some such equation as

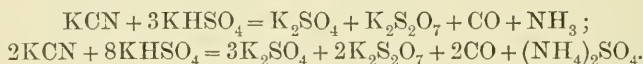


But the change is equally well brought about by a mixture of two volumes of concentrated sulphuric acid with one of Nordhausen acid, in which water can hardly be present, and it is therefore probable that part, at all events, of the latter is derived from the acid sulphate. This point would scarcely be worth attention, were it not that potassium hydrogen sulphate itself behaves in a closely parallel manner.

On heating an intimate mixture of the dry salt with dry potassium cyanide in an air bath at 230—250°, anhydrous hydrogen cyanide distils over, and may be collected in the apparatus described above, the yield corresponding with about 55 per cent. of the total cyanogen; this, of course, is the action which would naturally be expected,



But a large amount of carbon monoxide is also evolved at all stages of the action, and the residue left in the flask after the action has ceased smells strongly of ammonia, and dissolves in water, forming a strongly alkaline solution. As this carbon monoxide and ammonia are formed by the interaction of anhydrous substances, the hydrolytic water is necessarily derived from the potassium hydrogen sulphate, in accordance with such equations as the following:



It would thus appear that both sulphuric acid and potassium hydrogen sulphate can behave at the same instant and under the same conditions both as hydrolytic, and as dehydrating agents.

Anhydrous potassium ferrocyanide, it may be mentioned, interacts with potassium hydrogen sulphate in a similar manner, about 40 per cent. of the cyanogen being converted into hydrogen cyanide, and about 10 per cent. into carbon monoxide and ammonia, the residual 50 per cent. remaining in combination as potassium ferrous ferrocyanide, as in the ordinary method of preparing dilute hydrocyanic acid. With excess of acid sulphate and at a high temperature, carbon and sulphur dioxides are evolved in abundance, as with the simple cyanides.

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## XXIV.—*Manganic Salts.*

By CHARLES EMMANUEL RICE, B.A.

SEVERAL salts of manganese derived from the oxide  $\text{Mn}_2\text{O}_3$  have been described, but they are all unstable, and decomposed by contact with

water, hydrated higher oxides of manganese being precipitated; the most stable salt seems to be the acetate,  $\text{Mn}(\text{C}_2\text{H}_3\text{O}_2)_3 + 2\text{H}_2\text{O}$ , obtained by Christensen (*J. pr. Chem.*, 1883, [ii], 28, 1). The salmon-coloured metaphosphate,  $\text{Mn}(\text{PO}_3)_3 + \text{H}_2\text{O}$ , has been obtained by Hermann (*Ann. Phys. Chem.*, 1848, 74, 303), and the pyrophosphate,  $\text{MnHP}_2\text{O}_7$ , by Lefèvre (*Compt. rend.*, 1890, 110, 405); Carius (*Annalen*, 1856, 98, 53) has obtained the sulphate  $\text{Mn}_2(\text{SO}_4)_3$ . The potassium and ammonium alums are also well known, but they are decomposed by contact with much water; a black double oxalate,  $\text{K}_6\text{Mn}_2(\text{C}_2\text{O}_3)_6 + 6\text{H}_2\text{O}$ , has been obtained by Kehrman (*Berichte*, 20, 1594); the nitrate appears to be unknown, but the fluoride,  $\text{MnF}_3 + 3\text{H}_2\text{O}$ , has been described by Christensen (*J. pr. Chem.*, 1887, 35, 57) together with double salts of the type  $2\text{M}'\text{F}, \text{MnF}_3$ , but so far, no other haloid compound of manganese in which the metal is more than bivalent. Nicklès (*Ann. Chim. Phys.*, [iv], 5, 161) claimed to have produced  $\text{MnCl}_4$ , but there is really no evidence for the existence of such a compound.

The action of hydrochloric acid on the higher oxides of manganese has attracted a good deal of attention in this connection, but the higher chloride of manganese which is supposed to exist in the dark-coloured solution has not so far been isolated. W. W. Fisher (*Trans.*, 1878, 33, 409) on diluting the liquid with water and weighing the precipitated peroxide, found that for each atom of manganese precipitated, two atoms of available chlorine (chlorine that will liberate iodine from potassium iodide) disappeared from the solution; from this he inferred the presence of a compound,  $\text{MnCl}_4$ . Pickering (*Trans.*, 1879, 35, 1, 654) showed that this could be equally well accounted for by the existence of a compound,  $\text{Mn}_2\text{Cl}_6$ ; and he offered further evidence in support of this formula by showing that when manganese dioxide is dissolved in presence of manganous chloride, the amount of dioxide precipitated on diluting with water increases, the increase being in a greater proportion up to the addition of one molecule of  $\text{MnCl}_2$ . This would seem to show that the chloride combines with the two atoms of chlorine set free when  $2\text{MnO}_2$  dissolves, forming a second molecule of  $\text{Mn}_2\text{Cl}_6$ . He also observed that  $\text{Mn}_2\text{O}_3$  dissolves in cold hydrochloric acid without effervescence through evolution of chlorine, whereas a marked effervescence always accompanies the dissolution of  $\text{MnO}_2$ . This has been repeatedly confirmed by me with acid saturated at  $-15^\circ$ , and it would appear that when  $\text{MnO}_2$  is acted on by hydrochloric acid, one atom of chlorine is at once set free for each atom of manganese present, and another subsequently on heating the liquid, due to decomposition of the manganic chloride in solution.

Pickering's experiments made it very probable that a compound,  $\text{Mn}_2\text{Cl}_6$  or  $\text{MnCl}_3$ , yielding chlorine and  $\text{MnCl}_2$  by dissociation, exists in the dark-coloured solution. He failed, however, to show

I. That the reaction is reversible, and, therefore, that a definite chlorinated compound really is formed and dissociated.

II. That this compound can be obtained in the solid state.

The following is a record of an experimental investigation of these problems.

I. Crystals of chlorine hydrate were sealed up in a tube with some hydrochloric acid solution of manganous chloride, the tube being allowed to remain at the ordinary temperature. No apparent change occurred for some hours, but gradually, in the course of a few days, the manganous chloride solution became dark-coloured owing to the synthesis of  $\text{MnCl}_3$ , the depth of colour eventually reaching a maximum. Evidently the velocity of the reaction  $\text{MnCl}_2 + \text{Cl} = \text{MnCl}_3$  is very slow. In the absence of acid, a deposit of higher oxide of manganese is formed. The same changes occur if a cooled solution of manganous chloride be saturated with chlorine at the atmospheric pressure and left for some days.

II. I have succeeded in obtaining two double chlorides containing the manganic chloride fairly pure and in well-defined crystals. About 50 grams of a higher oxide of manganese ( $\text{Mn}_2\text{O}_3$ ,  $\text{Mn}_3\text{O}_4$ ,  $\text{MnO}_2$ , or a mixture of any of these) was placed in a flask with 250 c.c. of cold concentrated hydrochloric acid, and the flask, placed in a freezing mixture of ice and salt, was saturated with dry hydrogen chloride. After the mixture had been left to stand in the freezing mixture for half-an-hour to allow particles of undissolved oxide to settle, the fairly clear upper half was decanted, and a few c.c. of a slightly warmed saturated acidified solution of ammonium chloride was added to it drop by drop. The liquid was then replaced in the freezing mixture, resaturated with hydrogen chloride, and, after the lapse of about half an hour, filtered through a cooled Gooch crucible. The mass of small, dark, lustrous crystals left on the filter was washed with a few drops of cold saturated hydrochloric acid, drained on a porous plate, and left in a desiccator over soda-lime for some days under reduced pressure.

The crystals are perfectly transparent under the microscope, transmitting a ruby-coloured light. They have a slightly pungent odour, and may be raised to a temperature of  $100^\circ$  without perceptible change; above that temperature, however, they evolve chlorine and water, and, if heated in a current of air, leave a white residue of manganous chloride and ammonium chloride. They dissolve in hydrochloric acid, yielding a liquid resembling that from which they were obtained. Water at once decomposes them, about half the total manganese separating as hydrated higher oxide, and half remaining in solution as manganous chloride. Analysis gave results which correspond with the formula  $\text{MnCl}_3 \cdot 2\text{NH}_4\text{Cl} + \text{H}_2\text{O}$ .



	Mn.	Cl.	NH <sub>4</sub> .	H <sub>2</sub> O (by difference).
Calculated .....	19.1	61.9	12.6	6.3
Found .....	19.1	62.1	12.2	6.6

The ratio of Mn to Cl atoms is 1:5; from the formula one would expect one of these atoms, or 12.4 per cent. of chlorine, to be "loose," or available for oxidising purposes. It was found, on treatment with potassium iodide, that 12.6 per cent. available chlorine was present in the crystals.

The potassium salt,  $\text{MnCl}_3 \cdot 2\text{KCl} + \text{H}_2\text{O}$ , was obtained in the same way, and all its properties were found to be very similar. The water was determined directly in this salt, whereas in the ammonium compound it was estimated by difference. The analytical results, the average of three separate analyses, are as follows.

	Mn.	Cl.	K.	H <sub>2</sub> O.	Cl (loose).
Calculated...	16.7	54.0	23.8	5.5	10.8
Found .....	16.8	53.7	23.6	5.9	10.7

Several attempts have been made to isolate the manganic chloride itself, but so far without success. When heated in a current of gaseous hydrochloride or chlorine, the double salts decompose, yielding water and chlorine, and leaving a residue of manganous chloride and alkali chloride. With cold sulphuric acid, they evolve hydrogen chloride and chlorine, manganous sulphate being deposited; on mixing them with phosphoric anhydride, a manganic phosphate resembling permanganic acid in colour is produced.

The above salts are apparently isomorphous with the corresponding compounds of ferric chloride,  $\text{FeCl}_3 \cdot 2\text{NH}_4\text{Cl} + \text{H}_2\text{O}$  and  $\text{FeCl}_3 \cdot 2\text{KCl} + \text{H}_2\text{O}$ , which form monoclinic crystals with triangular faces, resembling those of octahedra; they help, therefore, to draw closer the relationship between iron and manganese. From the position of manganese in the series, whether it be placed with the iron group or with the halogens, we should hardly expect it to form quadrivalent compounds of the type  $\text{MnCl}_4$ .

The dark, chlorine-generating solution is a solution of manganic chloride,  $\text{MnCl}_3$ , and there is no evidence for the existence of any other compound, besides the dioxide, in which the manganese is in the quadrivalent state.

The author wishes to express his indebtedness to Professor Tilden, under whose superintendence these experiments have been carried out.

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XXV.—*Chemical Properties of Concentrated Solutions of certain Salts. Part I. Double Potassium Carbonates.*

By WILLIAM COLEBROOK REYNOLDS, A.R.C.S.

IN the course of some experiments on the preparation of potassium percarbonate recently discovered by Messrs. Constam and Von Haussen (*Zeit. fur Elektrochem.*, 1897, p. 455, and *Moniteur Sc.*, August, 1897), I noticed that copper sulphate would dissolve in the concentrated solution of potassium carbonate employed, yielding a deep blue liquid; as nothing appeared to be known about the compound thus formed, attempts were made to isolate it.\* It was soon found that the salts of several other metals will also dissolve in this solution to a greater or less extent, and that from such solutions crystalline compounds could in most cases be obtained which on analysis proved to be double carbonates.

Most of the information we possess about the double carbonates we owe to Deville (*Ann. Chim. Phys.*, [iii], 33), who found that by digesting metallic nitrates with a saturated solution of potassium hydrogen carbonate at the ordinary temperature, compounds of the type  $MKH(CO_3)_2$  were formed, where M is cobalt, nickel, or magnesium, and that if the solutions are heated for some hours they passed into  $MK_2(CO_3)_2$ ; he also obtained the sodium double salts of the latter type with cobalt, nickel, copper, and magnesium.

As the result of a large number of experiments, I find that the best general method of preparing the compounds is the following. To the concentrated solution of potassium carbonate (sp. gr. about 1.55) the finely powdered acetate is added and the solution set aside; the crystals which form are then separated from the mother liquor by draining on a disc of toughened filter paper placed on a Buchner filter plate, employing a water pump to diminish the pressure beneath. The crystals are washed with a mixture consisting of two volumes of alcohol and one of glycerol (which floats on the salt solution and does not mix with it) until all the mother liquor is displaced, when the washing is completed with alcohol only until all the glycerol is removed.

The crystals can be dried in a vacuum at the ordinary temperature over sulphuric acid.

The acetates are most convenient as, owing to the solubility of potassium acetate, the deposition of crystals of other potassium salts

\* The solutions of copper potassium carbonate introduced by Soldaini (*Gazzetta*, 1876, 6, 322) and afterwards modified by Ost (*Ber.*, 1890, 23, 1035 and 3003) for use in sugar analysis contain potassium hydrogen carbonate.

can be avoided. The freshly precipitated carbonates and hydrated basic carbonates have been used in several cases, but their employment is attended with some difficulty.

These compounds are decomposed by water alone, more or less rapidly, and alcohol alone causes the deposition of potassium carbonate upon the surface of the crystals of the new salt; hence the necessity for the use of the mixture already referred to. In one case, however, namely, that of the ferric salt, this mixture was found to decompose the compound and petroleum was substituted for it, as, notwithstanding its lower density and immiscibility with aqueous liquids, it served to displace the mother liquid.

*Copper Potassium Carbonate.*—This is very soluble in the strong solution, and a considerable quantity of copper acetate has to be added to get any crystals. The salt crystallises in three ways, namely, in the anhydrous form, with  $1\text{H}_2\text{O}$  and with  $4\text{H}_2\text{O}$ ; the three forms can be obtained from the same solution, provided the right proportions are employed. Thus, a solution made by adding to 70 c.c. of potassium carbonate solution of sp. gr. 1.35, 13 grams of finely powdered copper acetate, at  $65^\circ$ , filtering and cooling, deposited, after 48 hours, (a) dark, blue six-sided plates of the anhydrous salt, (b) light blue, silky, clustered needles of the salt with  $1\text{H}_2\text{O}$ , and (c) large greenish-blue, square tables of the salt with  $4\text{H}_2\text{O}$ . The last could be picked out by hand and freed from the liquid by means of filter paper. The compounds (a) and (b) appear to be deposited indifferently from solutions of the same strength and temperature, and I have not been able to find the conditions under which the individual compound could be obtained with certainty.

To prepare (a) or (b), the solution of potassium carbonate (sp. gr. 1.53) is added to the finely powdered copper acetate in a mortar, and after being triturated a few seconds to break up any lumps, when practically all dissolves, it is filtered rapidly through glass wool and set aside. A mixture of 36 grams of the acetate and 100 c.c. of the solution begins to crystallise in 2 or 3 minutes, and after about 10 minutes those crystals which have been formed should be separated and the remainder in two or three fractions, to prevent the solution becoming clogged. Thirty grams and 100 c.c. and separation in two instalments; or 17 grams and 100 c.c. all at once, are convenient quantities. The proportion of 12 grams to 100 c.c. generally requires some hours before crystals appear.

Analysis of the anhydrous compound (a dark blue, crystalline powder).

	$\text{CO}_2$ .	$\text{CuO}$ .	$\text{K}_2\text{O}$ .	$\text{H}_2\text{O}$ .
Found .....	32.92	31.54	35.39	0.06
Calculated for $\text{CuK}_2(\text{CO}_3)_2$ .....	33.67	30.31	36.02	nil.

Analysis of the light blue, silky needles.

	CO <sub>2</sub> .	CuO.	K <sub>2</sub> O.	H <sub>2</sub> O (by diff.).
Found.....	30.77	29.93	32.70	6.60
Calculated for CuK <sub>2</sub> (CO <sub>3</sub> ) <sub>2</sub> + H <sub>2</sub> O...	31.45	28.41	33.70	6.44

(Specimens (a) and (b) probably were contaminated with a little hydrated copper carbonate.)

Analysis of the greenish-blue tables.

	CO <sub>2</sub> .	CuO.	K <sub>2</sub> O.	H <sub>2</sub> O (by diff.).
Found.....	26.24	23.14	28.84	21.78
Calculated for CuK <sub>2</sub> (CO <sub>3</sub> ) <sub>2</sub> + 4H <sub>2</sub> O	26.39	23.78	28.26	21.57

The copper solution decomposes slowly when heated to 65°, and rather quickly at 85°, cupric oxide being precipitated; if, however, a large quantity of the acetate is added, no black precipitate forms even at 100°, but a green powder of the composition Cu<sub>2</sub>(OH)<sub>2</sub>CO<sub>3</sub>.

*Cobalt Potassium Carbonate.*—A cobalt salt dissolves in the warm solution of potassium carbonate and small six sided rose-coloured crystals soon separate on cooling.

	CO <sub>2</sub> .	CoO.	K <sub>2</sub> O.	H <sub>2</sub> O.
Found.....	26.30	22.78	28.70	22.10
Calculated for CoK <sub>2</sub> (CO <sub>3</sub> ) <sub>2</sub> + 4H <sub>2</sub> O	26.72	22.78	28.64	21.86

*Nickel Potassium Carbonate.*—A nickel salt dissolves as above, but in much smaller quantity, and pale green crystals soon form on cooling.

	CO <sub>2</sub> .	NiO.	K <sub>2</sub> O.	H <sub>2</sub> O.
Found.....	26.68	22.64	28.82	21.86
Calculated for NiK <sub>2</sub> (CO <sub>3</sub> ) <sub>2</sub> + 4H <sub>2</sub> O	26.72	22.78	28.64	21.86

*Magnesium Potassium Carbonate.*—The magnesium compound is obtained in like manner, by adding magnesium acetate to the solution, crystals appear in a few minutes.

	CO <sub>2</sub> .	MgO.	K <sub>2</sub> O.	H <sub>2</sub> O (by diff.).
Found.....	29.74	14.15	32.02	24.09
Calculated for MgK <sub>2</sub> (CO <sub>3</sub> ) <sub>2</sub> + 4H <sub>2</sub> O	29.86	13.72	32.00	24.42

The last three are identical with the compounds obtained by Deville by prolonged heating with a saturated solution of potassium hydrogen carbonate.

*Manganese Potassium Carbonate.*—The last three salts are best prepared from warm solutions, but this one must be prepared at the ordinary temperature, otherwise much oxidation occurs. The acetate was powdered in a mortar, and the solution added and stirred for a few seconds; the crystals separate out very quickly, as the salt is scarcely soluble in the solution.

	CO <sub>2</sub>	MnO.	K <sub>2</sub> O.	H <sub>2</sub> O.
Found.....	26·86	21·80	29·20	22·14
Calculated for MnK <sub>2</sub> (CO <sub>3</sub> ) <sub>2</sub> + 4H <sub>2</sub> O	27·03	21·82	29·03	22·12

*Ferrous Potassium Carbonate.*—In order to prevent oxidation, this salt must be prepared by a slight modification of the process. The following answered very well. A bottle containing about five-sixths of its volume of the solution was filled up with a saturated solution of ferrous chloride and stoppered; on mixing the two liquids by shaking, a white precipitate of FeCO<sub>3</sub> is at first formed, but this soon dissolves yielding a greenish solution, from which the compound FeK<sub>2</sub>(CO<sub>3</sub>)<sub>2</sub> + 4H<sub>2</sub>O crystallises out in nearly white scales after about 10 minutes. The salt can be separated and purified in the manner already described.

	CO <sub>2</sub>	FeO.	K <sub>2</sub> O.	H <sub>2</sub> O (by diff.).
Found.....	26·80	21·93	28·60	22·67
Calculated for FeK <sub>2</sub> (CO <sub>3</sub> ) <sub>2</sub> + 4H <sub>2</sub> O	26·99	22·06	28·89	22·06

*Calcium Potassium Carbonate.*—This can be easily prepared by pouring the solution on to the finely powdered acetate in a mortar and triturating for some time. The crystals are anhydrous, CaK<sub>2</sub>(CO<sub>3</sub>)<sub>2</sub>, and are quite different in form from the last five compounds, which contain water.

	CO <sub>2</sub>	CuO.	K <sub>2</sub> O.
Found .....	36·55	22·40	38·94
Calculated for CuK <sub>2</sub> (CO <sub>3</sub> ) <sub>2</sub> .....	37·00	23·50	39·50

(The salt probably retained about 2 per cent. moisture.)

*Silver Potassium Carbonate.*—This can be prepared by adding powdered silver nitrate to the solution, but I found it better to add the saturated solution of the nitrate to a large excess of the potassium carbonate solution, as in the former case particles of the nitrate which have become coated over with the compound are liable to be mixed with it. The yellow precipitate at first formed soon changes into the white double salt, AgKCO<sub>3</sub>. If exposed to light during the washing, superficial reduction takes place, due to the glycerol.

	CO <sub>2</sub>	Ag <sub>2</sub> O.	K <sub>2</sub> O.
Found .....	20·58	54·50	23·90
Calculated for AgKCO <sub>3</sub> .....	21·23	56·01	22·76

This salt has been already obtained by De Schulten (*Compt. rend.*, 1887, 105, 811).

*Bismuth Potassium Carbonate.*—When powdered bismuth nitrate is added to the solution, some effervescence occurs, but a considerable quantity slowly but completely dissolves; the crystalline compound that separates after a short time is mixed with crystals of potassium



nitrate and hydrogen carbonate from which it cannot be separated. It was found better, therefore, to employ the subnitrate. The crystals, which are microscopic, when prepared at the ordinary temperature are of an entirely different form from those obtained by adding the powder to the solution warmed to about  $75^{\circ}$ ; they have, however, the same composition. The commercial subnitrate contains a small quantity of a constituent which is not acted on by the solution. Most of this impurity can be got rid of by pouring the solution, after the addition of the subnitrate, into a tall cylinder and decanting from the impurity which settles down more quickly than the fine crystals. A purer product can be obtained by preparing the subnitrate from the nitrate using a small quantity of water, draining with the aid of the filter pump, and adding the precipitated salt to the concentrated solution heated to about  $70^{\circ}$ . The crystals separate almost immediately.

	$\text{Bi}_2\text{O}_3$ .	$\text{K}_2\text{O}$ .	$\text{CO}_2$ .	$\text{H}_2\text{O}$ (by diff.).
Found .....	55.00	21.86	20.26	2.88
Calculated for $\text{Bi}_2\text{OK}_4(\text{CO}_3)_4 + \text{H}_2\text{O}$	54.90	22.24	20.73	2.13

The following list contains all the salts I have been able to isolate in well-defined crystalline form.

$\text{CuK}_2(\text{CO}_3)_2$ .....	}	Not previously known.
$\text{CuK}_2(\text{CO}_3)_2 + \text{H}_2\text{O}$ .....		
$\text{CuK}_2(\text{CO}_3)_2 + 4\text{H}_2\text{O}$ .....		
$\text{MnK}_2(\text{CO}_3)_2 + 4\text{H}_2\text{O}$ .....		
$\text{FeK}_2(\text{CO}_3)_2 + 4\text{H}_2\text{O}$ .....		
$\text{CaK}_2(\text{CO}_3)_2$ .....	}	Obtained by Deville by heating the bicarbonate.
$\text{Bi}_2\text{OK}_4(\text{CO}_3)_4 + \text{H}_2\text{O}$ .....		
$\text{CoK}_2(\text{CO}_3)_2 + 4\text{H}_2\text{O}$ .....		
$\text{NiK}_2(\text{CO}_3)_2 + 4\text{H}_2\text{O}$ .....		
$\text{MgK}_2(\text{CO}_3)_2 + 4\text{H}_2\text{O}$ .....		
$\text{AgK}(\text{CO}_3)$ .....		Obtained by De Schulten.

In addition to these, I have obtained compounds containing lead, zinc, iron (ferric) chromium, mercury, and cadmium, but not crystalline or of definite composition.

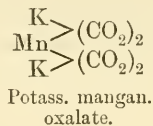
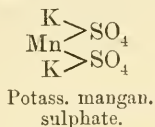
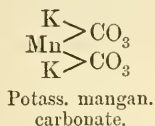
It is noticeable that the chemical behaviour of potassium carbonate in the form of a concentrated solution is quite different from that of the same salt in a dilute solution. In the latter case, normal or basic carbonates are formed, whereas, in the former, double salts are produced which may be soluble in the liquid.

The solutions and the compounds in the solid state are decomposed when diluted or brought into contact with water; in this respect, they are similar to the double sulphates, which are all decomposed by water. In the case of such compounds as  $\text{CaNa}_2(\text{SO}_4)_2$  and  $\text{CaK}_2(\text{SO}_4)_2$ , this is



evident, since calcium sulphate is precipitated, but in the case of the soluble salts, although not so obvious, the fact of decomposition has been proved by Raoult (*Compt. rend.*, 1884, 99, 914), and also from thermochemical data.

It is noticeable that the ratio of K to  $\text{CO}_3$  is unity in all the above compounds, and this is also the case with the double sulphates  $\text{K} : \text{SO}_4$ , and double oxalates  $\text{K} : (\text{CO}_2)_2$ , and it is possible to write the constitution of these three classes of double salts thus.



A concentrated solution of potassium succinate behaves very like that of potassium carbonate; although the succinates of the metals, except the alkalis, are almost insoluble, yet on adding their salts to a concentrated solution of potassium succinate many of them dissolve, and crystalline double compounds are obtainable. I propose to give an account of these in a future communication.

The above investigation was carried out under the supervision of Professor Tilden, to whom I am much indebted for his advice and encouragement.

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## XXVI.—*The Colouring Matters of the Indian Dye Stuff Asbarg, Delphinium zaili.*

By ARTHUR GEORGE PERKIN, F.R.S.E., and JULIUS ALDRED PILGRIM.

ASBARG consists of the dried flowers and flowering stems of *Delphinium zaili*, a perennial, herbaceous plant belonging to the *Ranunculaceae*, which is found in great quantity in Afghanistan. Dr. Aitchison says of it (*Watts' Dictionary of the Economic Products of India*, 1890, 3, p. 70): "This plant forms a great portion of the rolling downs of the Badghis; in the vicinity of Gulran it was in great abundance and when in blossom gave a wondrous golden hue to the pastures; in many localities in Khorassan of about 2000 feet altitude, it is equally common."

The dried fragments and flowering stems are taken to Multan and other Punjab towns, from which they are conveyed all over India. It is much used in silk dyeing for the production of a sulphur-yellow colour known as "gandhaki," and together with *Datisca cannabina* to

obtain a similar shade on alum mordanted silk; it is also used in calico printing. The flowers, which are bitter, are likewise employed medicinally as a febrifuge.

No examination of the colouring matter of this dye stuff appears to have been previously made, although an account of its tinctorial properties has been communicated to the Society of Chemical Industry (*J. Soc. Ch. Ind.*, 1895, 14, 458) by J. J. Hummel and one of us. Our thanks are due to the authorities of the Imperial Institute, who, on the application of Professor Hummel, were good enough to procure a considerable quantity of this material for our investigation.

### EXPERIMENTAL PART.

At the commencement of this investigation, the flowers and flowering stems of the plant were examined together, but the latter, being practically devoid of dyeing property, were subsequently discarded, an economy of labour being thus effected. Various methods suggested themselves for the isolation of the colouring matter, which exists here entirely as a glucoside, and ultimately the following was adopted.

The dye stuff was extracted with ten times its weight of boiling water, the mixture strained through calico, and the filtrate, after treatment with a little sulphuric acid, was again boiled for 15 minutes. The decomposition of the glucosides is very readily effected, and the action should not be prolonged, otherwise a tarry product is formed, which is a great hindrance in the later processes. On cooling, a brownish-yellow powder separated, which was collected, drained upon a porous tile, and when dry digested with boiling alcohol which dissolved the colouring matter, leaving a considerable residue of calcium sulphate. The dark coloured solution, after being evaporated to a small bulk, was poured into a large volume of ether, the mixture washed with water until the washings were colourless, and then agitated with dilute alkali to free the substance from a wax which alone remained in the ether after this treatment. On acidifying the alkaline liquid, it deposited yellow flocks of the colouring matter still contaminated with some impurity of an acid nature; to remove this, excess of sodium hydrogen carbonate was added to the mixture, and the product extracted with ether; this now dissolved nothing but the colouring matter, and the latter, on evaporation, was left of a pure yellow colour.

#### *Sparingly soluble Colouring Matter.*

It was evident on examination that the product thus obtained contained two colouring matters at least, one of which was distinguished by its sparing solubility in alcohol. After being isolated by this means it was converted into its acetyl derivative, which was recrystal-

lised, and then decomposed in the usual manner, the regenerated colouring matter being finally crystallised from acetic acid.

0.1164 gave 0.2598  $\text{CO}_2$  and 0.0400  $\text{H}_2\text{O}$ .  $\text{C} = 60.86$  ;  $\text{H} = 3.81$ .

$\text{C}_{16}\text{H}_{12}\text{O}_7$  requires  $\text{C} = 60.76$  ;  $\text{H} = 3.79$  per cent.

It formed a glistening mass of yellow needles, resembling rhamnetin in appearance, very sparingly soluble in boiling alcohol or acetic acid. With lead acetate in alcoholic solution, an orange-red precipitate was formed, whilst ferric chloride gave a greenish-black coloration. With the haloid acids, in the presence of acetic acid, no compounds of the acids were produced; sulphuric acid also reacted with difficulty, and owing to the small yield and the instability of the product thus obtained, it was not further examined.

*Fusion with Alkali.*—The colouring matter was digested with very concentrated potassium hydroxide solution at  $200\text{--}220^\circ$  for 1 hour, and the brown melt dissolved in water; the green solution was then neutralised with acid, extracted with ether, and the extract evaporated. The residue, after being dissolved in water, was treated with lead acetate, and the yellowish-white precipitate thus produced was collected, washed, and decomposed with dilute sulphuric acid. From the clear liquid, ether extracted a crystalline acid, soluble in dilute alkali to form a green liquid which became brown on exposure to air. The acid was now dissolved in water, and the solution saturated with salt, causing the separation of a trace of a viscous product which was removed by filtration. The filtrate was extracted with ether, and the residue obtained on evaporation purified by crystallisation from water. With dilute alkali, this product now yielded a colourless solution, and examination showed that the green coloration previously obtained in this manner was due to the impurity removed by the salt treatment.

0.1135 gave 0.2275  $\text{CO}_2$  and 0.0400  $\text{H}_2\text{O}$ .  $\text{C} = 54.66$  ;  $\text{H} = 3.91$ .

$\text{C}_7\text{H}_6\text{O}_4$  requires  $\text{C} = 54.54$  ;  $\text{H} = 3.90$  per cent.

It crystallised in colourless needles melting at  $194\text{--}196^\circ$ , gave a green coloration with aqueous ferric chloride, and evidently consisted of *protocatechuic acid*.

The filtrate from the lead precipitate was treated with sulphuric acid, filtered from lead sulphate, neutralised with sodium hydrogen carbonate, and extracted with ether. The crystalline residue left on evaporation, when purified, melted at  $210^\circ$ , and was found to be *phloroglucinol*.

The substance which gave the green coloration when the melt was dissolved in water could not be isolated in a pure condition, the quantity present being very small. In a second experiment, employing a new preparation of the colouring matter, this substance was

not detected, and it was thought that the green coloration had been due to an impurity. It appeared subsequently, however, that the condition necessary for its production was the use at the first of a comparatively dilute caustic alkali solution, preferably four parts of alkali in one of water. It is evident, therefore, that the reaction is characteristic of this colouring matter.

*Action of Hydriodic Acid.*—The similarity of this substance to rhamnetin, especially in its behaviour towards mineral acids, suggested that it contained a methoxy-group. Examination by Zeisel's method proved this to be the case.

0.1750 gave 0.1310 AgI.  $\text{CH}_3 = 4.77$ .

$\text{C}_{15}\text{H}_9\text{O}_6(\text{OCH}_3)$  requires  $\text{CH}_3 = 4.74$  per cent.

To the hydriodic acid residue, after dilution with water, sodium hydrogen sulphite solution was added, and the yellow, flocculent product collected and crystallised from dilute alcohol.

0.1021 gave 0.2242  $\text{CO}_2$  and 0.0345  $\text{H}_2\text{O}$ .  $\text{C} = 59.88$ ;  $\text{H} = 3.75$ .

$\text{C}_{15}\text{H}_{10}\text{O}_7$  requires  $\text{C} = 59.60$ ;  $\text{H} = 3.31$  per cent.

The product from a second experiment was acetylated, and the colourless substance, which melted at  $189-191^\circ$ , was analysed.

0.1165 gave 0.2494  $\text{CO}_2$  and 0.0462  $\text{H}_2\text{O}$ .  $\text{C} = 58.38$ ;  $\text{H} = 4.40$ .

$\text{C}_{15}\text{H}_5\text{O}_7(\text{C}_2\text{H}_3\text{O})_5$  requires  $\text{C} = 58.59$ ;  $\text{H} = 3.90$  per cent.

The above results, and the fact that the methyl ether when fused with alkali gives phloroglucinol and protocatechuic acid, indicated that this substance,  $\text{C}_{15}\text{H}_{10}\text{O}_7$ , was *quercetin*. An examination of its general properties corroborated this view. It is thus evident that the sparingly soluble colouring matter of *Delphinium zabil* is a *quercetin monomethyl ether*.

*Acetyl Compound.*—To confirm the above results, and to determine if this colouring matter was identical with either of the two known methyl ethers of quercetin (rhamnetin and iso-rhamnetin), it was acetylated in the usual manner, and the product crystallised from alcohol.

0.1213 gave 0.2650  $\text{CO}_2$  and 0.0445  $\text{H}_2\text{O}$ .  $\text{C} = 59.57$ ;  $\text{H} = 4.07$ .

$\text{C}_{16}\text{H}_8\text{O}_7(\text{C}_2\text{H}_3\text{O})_4$  requires  $\text{C} = 59.50$ ;  $\text{H} = 4.13$  per cent.

A determination of the methoxy-group gave the following result.

0.2076 gave 0.0880 AgI.  $\text{CH}_3 = 2.70$ .

Theory requires  $\text{CH}_3 = 3.09$  per cent.

Liebermann's method was employed for the estimation of the acetyl groups.



1.0740 gave 0.7047  $C_{16}H_{12}O_7$ . Found 65.61.

The theory for four acetyl groups requires  $C_{16}H_{12}O_7 = 65.29$  per cent.

It formed a glistening mass of colourless, hair-like needles, melting at  $195-196^\circ$ , identical in appearance and general properties with acetyliso-rhamnetin. The sparingly soluble colouring matter of the *Delphinium zalil* is, therefore, *iso-rhamnetin*, a substance but recently isolated for the first time (Trans., 1896, 69, 1650) from the petals of the yellow wallflower (*Cheiranthus Cheiri*). The difficulty of obtaining a sufficient supply of raw material did not allow at that time of the determination of the position of the methoxyl group in this colouring matter. Experiments were, therefore, now instituted with this object.

*Methylation of Iso-rhamnetin*.—As in the case of rhamnazin (quercetin dimethyl ether) (Trans., 1897, 818), this reaction was studied, for should the methoxy-group be present in the ortho-position relatively to the carbonyl group, a quercetin pentamethyl ether might be produced, and not the tetramethyl compound, which is always formed when quercetin itself is so treated.

Iso-rhamnetin (1 mol.) dissolved in a solution of potassium hydroxide (4 mols.) in methylic alcohol was digested with excess of methylic iodide for 24 hours. After removal of the unattacked iodide and excess of alcohol, the residue was dissolved in ether, and the solution washed with dilute alkali and evaporated; the product, after crystallisation from acetone, formed pale yellow needles melting at  $154-156^\circ$ .

0.1170 gave 0.2745  $CO_2$  and  $0.0543\frac{1}{2}H_2O$ .  $C = 63.98$ ;  $H = 5.15$ .

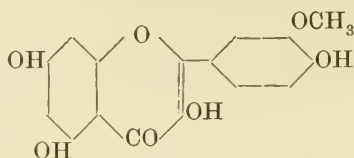
$C_{15}H_6O_3(OCH_3)_4$  requires  $C = 63.69$ ;  $H = 5.03$  per cent.

It was found to consist of *quercetin tetramethyl ether*.

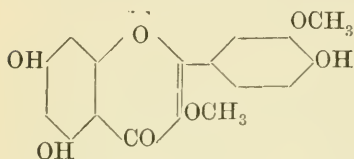
*Oxidation of Iso-rhamnetin*.—The previous experiment having given a negative result, it was necessary to determine if the methoxyl group was present in the catechol nucleus. For this purpose, air was aspirated through a dilute alkaline solution of the colouring matter until this, which was at first yellow, had become brown, and on treatment with acids no longer yielded a precipitate; the liquid was then neutralised with acid, treated with excess of sodium hydrogen carbonate, extracted with ether (A), and again acidified and extracted with ether (B). The latter extract, on evaporation, deposited crystals which were purified by recrystallisation from water until colourless; a lustrous mass of needles was thus obtained, which dissolved sparingly in cold water, gave no reaction with ferric chloride, and melted at  $206-207^\circ$ . This substance was *vanillic acid*, and the locality of the methoxy-group in iso-rhamnetin is thus evident. On evaporating extract (A), a residue was left having the reactions of *phloroglucinol*.



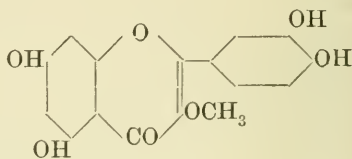
Employing the constitution assigned to quercetin by Herzig, that of iso-rhamnetin may be expressed as follows.



Consequently rhamnazin (*loc. cit.*), a quercetin dimethyl ether, is closely related to iso-rhamnetin and to rhamnetin, it being a mono-methyl ether of both these colouring matters.



Rhamnazin.



Rhamnetin.

*Dyeing Properties.*—A comparison was made of the tinctorial properties of iso-rhamnetin and quercetin, woollen cloth mordanted with aluminium, tin, chromium, and iron being employed for this purpose. The shades obtained were as follows.

	Aluminium.	Tin.	Chromium.	Iron.
Iso-rhamnetin	Lemon yellow.	Orange yellow.	Orange brown.	Pale brown olive.
Quercetin ...	Brown orange, inclining to yellow.	Bright orange.	Red brown.	Green black.

These results are interesting, as they indicate the effect of neutralising the two ortho-hydroxyls of quercetin by the conversion of one of them into a methoxy-group. As previously discussed (*Trans.*, 1897, 71, 818), the presence of these hydroxyls in quercetin enhances its tinctorial value, although iso-rhamnetin is again an instance that such a property is not essential to the dyes of this group. The shades produced are weaker than those given by quercetin, but considerably stronger than those given by rhamnazin, which is a very feeble dye; they somewhat closely resemble, especially in the yellow tint with aluminium mordant, that yielded by chrysin and apigenin in a similar way. Unlike these latter, however, it is capable of dyeing with a tin mordant. It is interesting to note that little evidence is now required for a complete study of the shade effect caused by the various hydroxyls existing in quercetin.

*Readily soluble Colouring Matter.*

The alcoholic mother liquors obtained during the isolation and purification of the above colouring matter were evaporated to half their bulk, and the small quantity of impure iso-rhamnetin which separated on long standing removed by filtration, and the filtrate treated with boiling water. On cooling, a yellow, crystalline product was deposited, which was collected and a portion acetylated, in the hope that this would lead to its identification. The colourless needles thus obtained had, however, no definite melting point, indicating a mixture, for they softened below  $100^{\circ}$ , and did not fuse completely until about  $160^{\circ}$ . It has been recently shown in a communication to the Society (Proc., 1898, 56), that various yellow colouring matters in alcoholic solution decompose potassium acetate with the production of insoluble salts, although this behaviour is not common to all of them. Fractional crystallisation having failed to effect a separation of these colouring matters, recourse was had to this reaction, in the hope that one only would form an insoluble product. A hot concentrated alcoholic solution of the substance was, therefore, boiled with a small quantity of potassium acetate for a few minutes, and the crystals which gradually separated were collected, washed with alcohol, and decomposed with acid. The regenerated colouring matter was further purified by suspending it in acetic acid and adding sulphuric acid, and the deposited acid compound was then collected, washed with acetic acid, and decomposed in the usual manner.

0.1200 gave 0.2620  $\text{CO}_2$  and 0.0410  $\text{H}_2\text{O}$ .  $\text{C} = 59.54$ ;  $\text{H} = 3.79$ .

$\text{C}_{15}\text{H}_{10}\text{O}_7$  requires  $\text{C} = 59.60$ ;  $\text{H} = 3.31$  per cent.

It formed glistening needles, an alcoholic solution of which gave an orange-red precipitate with lead acetate, and with ferric chloride a dark green coloration. The *acetyl compound* was obtained as colourless needles melting at  $189-191^{\circ}$ .

0.1182 gave 0.2518  $\text{CO}_2$  and 0.0425  $\text{H}_2\text{O}$ .  $\text{C} = 58.09$ ;  $\text{H} = 3.99$ .

$\text{C}_{15}\text{H}_5\text{O}_7(\text{C}_2\text{H}_3\text{O})_5$  requires  $\text{C} = 58.59$ ;  $\text{H} = 3.90$  per cent.

As fusion with alkali yielded *protocatechuic acid* and *phloroglucinol*, this colouring was evidently *quercetin*.

To obtain, if possible, some clue as to the nature of the substance previously associated with the quercetin and which did not react with potassium acetate, the filtrate from the potassium quercetin was first saturated with the acetate, any deposited salt thus produced being removed by filtration; the filtrate was then acidified, treated with boiling water, and the crystals which separated collected, washed, and dried. Experiments with this product gave results which indicated that

it was not homogeneous, but as the quantity available was very small no further attempts at purification could be carried out with advantage. On analysis, it yielded numbers  $C = 59.8$ ,  $H = 3.90$ , somewhat similar to those required for quercetin,  $C = 59.60$ ,  $H = 3.31$ . Its acetyl derivative, which formed colourless needles, behaved peculiarly when heated, for it fused entirely at  $118-120^\circ$ , then gradually solidified, and melted again at  $179-180^\circ$ . A portion which had melted at the lower temperature and again solidified, after recrystallisation, behaved in an identical manner. Analysis gave  $C = 58.54$ ,  $H = 4.24$ . Acetyl-quercetin requires  $C = 58.59$ ,  $H = 3.90$  per cent. On fusion with alkali, it yielded *phloroglucinol* and *protocatechuic acid*.

These results indicate a close similarity between this colouring matter and quercetin, and it would appear that it was merely the latter in an impure condition. Should this be the case, it is difficult to understand that so small an amount of impurity could account for its not giving an insoluble potassium salt when treated with potassium acetate, and also for the melting point of its acetyl derivative. Further study of this substance must be discontinued for the present, owing to the exhaustion of our supply of material.

#### *The Dyeing Properties of Asbarg.*

In the previous communication on this subject (*loc. cit.*), it was shown that a close resemblance exists in this respect between asbarg and quercitron bark, although the former yields, with aluminium mordant, a purer or less orange yellow. It is, however, a much weaker dye stuff, having but 35 per cent. the dyeing power of quercitron bark. As the above experiments were carried out with the material in the condition received from the Imperial Institute, further trials were instituted with a sample from which the worthless flowering stalks had been removed. The shades obtained with this product on wool mordanted in the usual manner are given below; they still indicated a lack of dyeing power as compared with quercitron bark.

	Aluminium.	Chromium.	Iron.	Tin.
Asbarg .....	Golden yellow.	Brownish orange.	Brown olive.	Bright orange.
Quercitron bark	Brown yellow.	Deep brown orange.	Olive black.	„

*Percentage of Colouring Matter.*—An examination of asbarg, minus the flowering stalks, showed that it contained 3.47 per cent. of colouring matter (not as glucoside). The estimation was carried out by a method we have lately devised for this purpose, and which we are

applying to the estimation of colouring matter in dye stuffs of the quercitron class. The details of the method are not given here, for we hope to make a communication on this subject at a later date.

An examination of the blue flowers of *Delphinium consolida* has shown that these contain, curiously enough, some quantity of yellow colouring matter; this, however, is not identical with that present in *Delphinium zaili*. The study of this product, which is at present delayed owing to lack of raw material, will be shortly continued.

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## XXVII.—*Researches on the Terpenes. II. On the Oxidation of Fenchene.*

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FENCHENE, which was first prepared and studied by Wallach (*Annalen*, 1891, 263, 130), is related to fenchone in the same way that camphene is to camphor. The derivatives of the fenchone and the camphor series show many points of analogy (*ibid.*, 269, p. 326, p. 347; *ibid.*, 275, p. 157; *ibid.*, 276, p. 315), and, at the same time, camphor is evidently closely related to turpentine hydrochloride (Armstrong, *Trans.*, 1896, 69, p. 1397). The present investigation was undertaken with the hope of deciding more definitely the relationship between these various compounds, and with this object we propose to study the oxidation of fenchone, fenchene, and turpentine hydrochloride by nitric acid, under conditions somewhat analogous to those employed by Marsh and Gardner in the oxidation of camphene (*Trans.*, 1896, 69, p. 74). In the present paper, we give some account of the oxidation products of fenchene, and of turpentine hydrochloride, from the former of which we have obtained, as a main product, camphopyric acid, and from the latter, camphoric and camphopyric acids. We mainly followed Wallach's methods in preparing fenchene from fenchone, but our experiences differ in several points from his, and we have introduced several modifications which we think it of interest to place on record.

*Fenchone*.—This was obtained by rectifying a fraction of fennel oil boiling at 170—230°, distilled for us by Schimmel and Co., and containing 40—50 per cent. of fenchone. The fraction boiling at 190—195° obtained from this sample by careful fractional distillation, and consisting mainly of fenchone, was purified by boiling with strong

nitric acid (sp. gr. 1.42) as Wallach directs. The product thus obtained, after being dried and distilled, was finally purified by freezing. It boiled constantly at 191—192°, melted at 6°, and had a specific rotatory power  $[\alpha]_D = +61^\circ 58'$  (not in solution).

This method of purification, although it yields very pure fenchone, is somewhat wasteful, as the fenchone is attacked slowly by the strong nitric acid.

*Fenchyl Alcohol.*—Wallach prepared the alcohol by the reduction of a solution of fenchone in absolute alcohol, by means of metallic sodium (*loc. cit.*, p. 143), but although we carefully followed his instructions, we did not get very satisfactory results, the reduction being slower and less complete than his account led us to expect. By using amylic alcohol instead of ethylic alcohol, the reduction took place much more completely, and we were able to operate easily on comparatively large quantities of material.

Two hundred grams of fenchone, dissolved in 1200 grams of amylic alcohol, was heated on the water bath, and 120 grams of sodium gradually added, a layer of sand having been placed at the bottom of the flask to prevent the melted sodium cracking the glass. When all the sodium had dissolved, which took from four to five hours, about  $1\frac{1}{2}$  volumes of water were added, and the supernatant layer of fenchyl and amylic alcohols was separated and distilled until the thermometer rose to 140°; the residue was then distilled in a current of steam, and the oil which came over dried with fused potassium carbonate and fractionated. The fractions boiling at 197—200°, which solidified in the condenser, consisted of pure fenchyl alcohol. It forms hard, white crystals, which melt at 45° and have a specific rotatory power  $[\alpha]_D = -13.37^\circ$  (in alcohol).

*Fenchyl Chloride.*—Wallach (*loc. cit.*, p. 148) prepared this compound by the action of phosphorus pentachloride on fenchyl alcohol in petroleum or chloroform solution, removing the chlorides of phosphorus, &c., by distillation under diminished pressure on the water bath, distilling the residue with steam, and finally fractionating under diminished pressure. We found it advantageous to remove the oxychloride of phosphorus by mixing the product with a large quantity of ice, and allowing it to stand, instead of distilling under diminished pressure, &c. The oil was then separated, dried, and distilled under a pressure of 20 mm., when the bulk of the liquid, consisting of fenchyl chloride, passed over at 85—90°. The yield was 83—84 per cent.

*Fenchene.*—Fenchene was prepared from the chloride by Wallach's method, namely, heating with aniline. The fenchene obtained, after careful fractionation, distilled mostly at 150—152°, with very small fractions 152—154°, 154—156°, 156—158°, 158—160°. The fraction 150—152°, on analysis, gave the following figures.



0.216 gave 0.6961  $\text{CO}_2$  and 0.2316  $\text{H}_2\text{O}$ . Found  $\text{C} = 87.89$ ;  $\text{H} = 11.9$ .  
Fenchene requires  $\text{C} = 88.21$ ;  $\text{H} = 11.76$  per cent.

A fraction boiling at  $150\text{--}154^\circ$  had a specific gravity 0.8667 at  $18^\circ$ , and a specific rotatory power  $[\alpha]_D = -6.46^\circ$  (not in solution).

*Phenylfenchylamine*.—After the fenchene obtained by the action of aniline on the chloride had been distilled over with steam, a thick black oil was left in the distilling flask\*; as it did not solidify, it was submitted to careful fractional distillation under a pressure of 13 mm., when the following fractions were obtained: below  $169^\circ$ ,  $169\text{--}171^\circ$ ,  $171\text{--}173^\circ$ ,  $173\text{--}175^\circ$ , and  $175\text{--}180^\circ$ , of which  $171\text{--}173^\circ$  was by far the largest; the latter, on analysis, gave the following numbers.

0.2054 gave 0.6305  $\text{CO}_2$  and 0.1919  $\text{H}_2\text{O}$ .  $\text{C} = 83.71$ ;  $\text{H} = 10.38$ .

0.3033 „ 16.4 c.c. nitrogen at  $20^\circ$  and 760 mm.  $\text{N} = 6.18$ .

0.2920 „ 16.5 c.c. „  $23^\circ$  „ 767 mm.  $\text{N} = 6.42$ .

$\text{C}_{10}\text{H}_{17}\cdot\text{NH}\cdot\text{C}_6\text{H}_5$  requires  $\text{C} = 83.84$ ;  $\text{H} = 10.04$ ;  $\text{N} = 6.12$  per cent.

This substance was a pale yellow, very viscous oil, which turned black on exposure to the air, but remained clear and transparent in a vacuum tube, and did not solidify when kept for many months, or by long standing in a freezing mixture of ice and salt. It seems to be isomeric with Wallach's substance.

*Action of Acetic Chloride on this Oil*.—Phenylfenchylamine, when mixed with an excess of acetic chloride, became hot; the mixture was heated for some time at  $100^\circ$ , the excess of acetic chloride distilled off, and the product distilled under a pressure of 24 mm., when most of it passed over at  $190\text{--}193^\circ$ . This acetyl derivative,  $\text{C}_{10}\text{H}_{17}\cdot\text{NPhAc}$ , was a very viscous, yellow oil, which did not solidify on long standing, or in a freezing mixture of ice and salt. It turned dark brown on exposure to air, but remained unchanged in a vacuum tube. It gave the following numbers on analysis.

0.1974 gave 0.5777  $\text{CO}_2$  and 0.1657  $\text{H}_2\text{O}$ .  $\text{C} = 79.80$ ;  $\text{H} = 9.32$ .

$\text{C}_{18}\text{H}_{25}\text{NO}$  requires  $\text{C} = 79.7$ ;  $\text{H} = 9.22$  per cent.

### *Oxidation of Fenchene.*

When fenchene, in portions of 20 grams, was heated on the water bath in a long-necked flask with 100 c.c. of water, and 100 c.c. of concentrated nitric acid added, a fairly vigorous reaction took place; after the action had considerably abated, 200 c.c. more nitric acid was added in quantities of 50 c.c. at a time whenever the action became very slow. After heating for 3 days on the water bath, the fenchene had entirely

\* In Wallach's experiments, this oil partially solidified, and the solid after repeated crystallisation from alcohol, melted at  $94^\circ$ . Analysis showed this to be fenchylphenylamine (*loc. cit.*, p. 150).

disappeared. The contents of the flask were then thoroughly distilled in a current of steam; the distillate contained a small quantity of an oil which solidified on standing, but which we have not yet obtained in sufficient quantity for investigation, and there were some acids in solution. The acid liquid was first neutralised with sodium carbonate, then made acid again by oxalic acid and distilled; acetic acid was recognised in the distillate by means of its silver salt.

The non-volatile residue left on distilling the oxidation product in steam was evaporated to a small bulk and left for a few days, when the yellow liquid deposited crystals; after the adhering oil had been removed by washing with chloroform, the crystals, which are insoluble in it, were purified by several recrystallisations from strong nitric acid and from water; they melted at  $207^{\circ}$ , and proved to be *cis*-camphopyric acid.

0.2102 gave 0.4465  $\text{CO}_2$  and 0.1460  $\text{H}_2\text{O}$ .  $\text{C} = 57.93$ ;  $\text{H} = 7.71$ .

$\text{C}_9\text{H}_{14}\text{O}_4$  requires  $\text{C} = 58.06$ ;  $\text{H} = 7.52$  per cent.

The oil remaining after the crystals of camphopyric acid had been separated was distilled under diminished pressure; a considerable amount of charring took place, and an oil and a solid substance distilled over. The former was an acid, but the latter neutral, so that they were easily separated by treatment with sodium carbonate solution; the solid was recrystallised from alcohol, and gave the characteristic crystals of *cis*-camphopyric anhydride melting at  $178^{\circ}$ .

On combustion, it gave the following figures.

0.2234 gave 0.5252  $\text{CO}_2$  and 0.1437  $\text{H}_2\text{O}$ .  $\text{C} = 64.12$ ;  $\text{H} = 7.14$ .

$\text{C}_9\text{H}_{12}\text{O}_3$  requires  $\text{C} = 64.28$ ;  $\text{H} = 7.14$  per cent.

The yield of camphopyric acid obtained in this way was just over 20 per cent.

We have not as yet been able to purify the acid oil which distilled over, but after neutralising with ammonia it gave a white, insoluble lead salt with lead acetate; this lead salt contained 60.7 per cent. of lead.

#### *Oxidation of Turpentine Hydrochloride.*

Turpentine hydrochloride, when oxidised on the water bath with nitric acid diluted with half its volume of water, was very slowly attacked; the greater portion slowly dissolved, leaving a heavy oil at the bottom of the flask, which was separated and oxidised by further treatment with nitric acid. On distilling the oxidised liquid in steam, acetic acid passed over, which was recognised by an analysis of its silver salt, whilst in the retort there remained, besides nitric acid, camphoric, camphopyric or camphoic and other acids.

The presence of camphoric acid was to be expected, as Armstrong some years ago obtained small quantities of this acid by oxidising turpentine hydrochloride with dilute nitric acid (1880 edition of Miller's *Chemistry*, also Trans., 1896, 69, p. 1398). In order to isolate the camphoric and camphoic or camphopyric acids, and as far as possible determine the quantities present, the above-mentioned residue was evaporated to dryness to get rid of nitric acid, taken up with ether, and extracted with sodium carbonate solution. The mixture of sodium salts thus obtained after being reconverted into the acids, was neutralised with caustic soda and precipitated with lead nitrate; the insoluble precipitate was then decomposed by sulphuric acid and extracted with ether. This solution, on long standing, gradually deposited a quantity of solid matter, which was crystallised from strong nitric acid, washed with chloroform, and again recrystallised from water. It melted at 199—200°. It was camphoric acid, and on combustion gave the following numbers.

0.2106 gave 0.4591 CO<sub>2</sub> and 0.1603 H<sub>2</sub>O. C = 59.46; H = 8.46.

C<sub>10</sub>H<sub>16</sub>O<sub>4</sub> requires C = 60. H = 8 per cent.

The acid, on treatment with acetyl chloride, was converted into the anhydride, which, after recrystallisation from alcohol and sublimation, melted at 217°. On analysis, it gave the following figures.

0.1994 gave 0.4804 CO<sub>2</sub> and 0.1421 H<sub>2</sub>O. C = 65.7; H = 7.9.

C<sub>10</sub>H<sub>14</sub>O<sub>3</sub> requires C = 65.92; H = 7.7 per cent.

This camphoric anhydride was then reconverted into the acid by dissolving it in caustic soda, and reprecipitating by hydrochloric acid. After crystallisation from water, it melted at 202—203°.

0.2011 gave 0.4414 CO<sub>2</sub> and 0.1487 H<sub>2</sub>O. C = 59.86; H = 8.21.

C<sub>10</sub>H<sub>16</sub>O<sub>4</sub> requires C = 60; H = 8 per cent.

The yield of camphoric acid from 300 grams of turpentine hydrochloride was 18 grams.

The oily mother liquors remaining after the separation of the deposit of camphoric acid, together with some oily matter obtained from the filtrate and wash waters from the lead salts, were submitted to distillation under a pressure of 20 mm. A considerable amount of charring took place, and a liquid passed over between 120° and 180°. The higher fraction of this (180—200°) for the most part solidified; this solid was purified by sublimation on an oil bath at 170°, and after recrystallisation from alcohol melted at 177—178°. These crystals had the characteristic form of *cis*-camphopyric anhydride. On combustion, the following results were obtained.

0.2140 gave 0.5024  $\text{CO}_2$  and 0.1418  $\text{H}_2\text{O}$ .  $\text{C} = 64.02$ ;  $\text{H} = 7.36$ .

0.1989 „ 0.4696  $\text{CO}_2$  „ 0.1305  $\text{H}_2\text{O}$ .  $\text{C} = 64.39$ ;  $\text{H} = 7.29$ .

$\text{C}_9\text{H}_{12}\text{O}_3$  requires  $\text{C} = 64.28$ ;  $\text{H} = 7.1$  per cent.

The yield of camphopyric anhydride was 9 grams from 300 grams of turpentine hydrochloride.

It is probable, in the light of the work of Gilles and Renwick on the oxidation of ketopinic acid (*Proc. Chem. Soc.*, 1897, pp. 64, 182) that this camphopyric acid was produced by the decomposition of camphoic acid, although we were unable to separate any camphoic acid from the crystalline part of the oxidation product.

We have as yet been unsuccessful in our attempts at purifying the accompanying oils.

The oxidation of fenchone under similar conditions takes place very much more slowly, and the products of this oxidation are at present under investigation.

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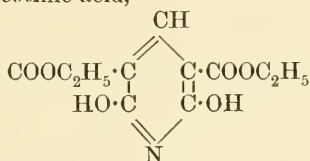
## XXVIII.—*Formation of Ethylic Dihydroxydinicotinate from Ethylic Cyanacetate.*

By SIEGFRIED RUHEMANN, Ph.D., M.A., and K. C. BROWNING, B.A.

THE experiments described in this paper have been undertaken with the view of investigating more closely the action of chloroform on ethylic malonate in presence of sodium ethoxide, as the yield of the sodium derivative of ethylic dicarboxyglutaconate thus obtained was found to be far from satisfactory, and in fact never reached that stated by Conrad and Guthzeit (*Annalen*, 1884, 222, 249), although this compound had been frequently prepared by one of us and his pupils. The mother liquor of this substance which had accumulated in the course of their researches served as material for this study.

The red-brown alcoholic filtrate from ethylic sodiodicarboxyglutaconate which, after concentration, did not yield any further crop of this substance, even when left for several weeks, deposited an oil when diluted with water; this was separated by the use of ether, and distilled under diminished pressure. Although the examination of this oil is not yet complete, it has been ascertained that it consists to a large extent of ethylic malonate. Excess of hydrochloric acid was added to the aqueous layer left after treatment with ether, and the solution again repeatedly shaken with ether; on distilling off the ether, a red

oil was left which did not deposit any solid on standing. When heated under diminished pressure, only a small quantity of a colourless liquid distilled at about  $150^{\circ}$ , but at  $160^{\circ}$  a reaction took place which resulted in the contents of the flask becoming a semi-solid mass of crystals; these were freed from the mother liquor by washing with dilute alcohol. The dark coloured product thus obtained contained inorganic matter and was only sparingly soluble in water or alcohol, but dissolved in cold concentrated hydrochloric acid. On adding water to this solution, an almost colourless, crystalline product was obtained which readily dissolved in alcohol, and crystallised from it in transparent needles melting at  $202^{\circ}$  to a red liquid. The compound, on examination, was found to contain nitrogen and to be the ethylic salt of dihydroxydinicotinic acid,



0.2040 gave 0.3855  $\text{CO}_2$  and 0.1000  $\text{H}_2\text{O}$ . C = 51.53; H = 5.44.

0.2400 „ 0.4510  $\text{CO}_2$  „ 0.1130  $\text{H}_2\text{O}$ . C = 51.25; H = 5.23.

0.2285 „ 0.4318  $\text{CO}_2$  „ 0.1045  $\text{H}_2\text{O}$ . C = 51.54; H = 5.08.

0.3084 „ 14.8 c.c. nitrogen at  $19^{\circ}$  and 769 mm.; N = 5.58.

$\text{C}_{11}\text{H}_{13}\text{NO}_6$  requires C = 51.76; H = 5.10; N = 5.49 per cent.

The compound is identical with that obtained by Guthzeit (*Ber.*, 1893, 26, 2795) from ethylic ethoxy- $\alpha$ -pyrinedicarboxylate and with the substance formed by heating ethylic dicarboxyglutaconate with formamide (Ruhemann and Sedgwick, *Ber.*, 1895, 28, 825). Guthzeit gives the melting point of this ethereal salt as  $199^{\circ}$ , whilst we found it to be  $202^{\circ}$  (as compared with  $201^{\circ}$  stated before, *loc. cit.*).

The formation of this pyridine derivative by the interaction of chloroform and ethylic disodiummalonate could only be explained by assuming that the ethylic malonate contained ethylic cyanacetate. Its presence might easily be accounted for by the circumstance that, in the preparation of ethylic malonate from chloracetic acid and potassium cyanide, and the subsequent action of alcohol and hydrogen chloride, a small quantity of the first formed ethylic cyanacetate remained unaltered.

With the view of verifying this explanation, we undertook the study of the action of chloroform on ethylic cyanacetate in the presence of sodium ethoxide. It was to be expected that this reaction would take place according to the equation  $2\text{CN} \cdot \text{CNa}_2 \cdot \text{COOC}_2\text{H}_5 + \text{CHCl}_3 = \text{COOC}_2\text{H}_5 \cdot \text{C}(\text{CN}) : \text{CH} \cdot \text{CNa}(\text{CN}) \cdot \text{COOC}_2\text{H}_5 + 3\text{NaCl}$ , and lead to the formation of the sodium compound of ethylic dicyanoglutaconate,

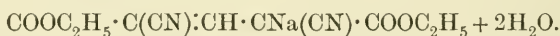


which in turn might be transformed into ethylic dihydroxydinicotinate. These reactions actually take place.

We had completed this enquiry when we noticed Errera's paper (*Gazzetta*, 1897, 27, ii, 393), which deals with the formation of ethylic dicyanoglutaconate and some of its derivatives.

*Ethylic Dicyanoglutaconate.*

The sodium derivative of this ethylic salt is prepared by a method similar to that used for ethylic dicarboxyglutaconate. To a solution of 9.2 grams of sodium in 150 grams of alcohol, 22.6 grams of ethylic cyanacetate and then 12 grams of chloroform are added; on heating the mixture on the water bath, the white precipitate of ethylic sodio-cyanacetate, first formed, becomes yellow, and after an hour's digestion the liquid is no longer alkaline to litmus. As the alcoholic solution can only with difficulty be freed by filtration from the gelatinous solid, the alcohol is distilled off, and water added to the residue, when the sodium derivative of ethylic dicyanoglutaconate remains undissolved. It is filtered from the dark coloured mother liquor, washed with water in which, in the cold, it is not very soluble, and twice recrystallised from boiling water; the long, yellow needles thus obtained, which, when dried in the air, contain  $2\text{H}_2\text{O}$  (as was also found by Errera, *loc. cit.*), have the formula



0.2460 (air dried) lost 0.0300 at  $100^\circ$ .  $\text{H}_2\text{O} = 12.19$ .

$\text{C}_{11}\text{H}_{11}\text{NaN}_2\text{O}_4 + 2\text{H}_2\text{O}$  requires  $\text{H}_2\text{O} = 12.24$  per cent.

0.2405 (dried at  $100^\circ$ ) gave 0.0652  $\text{Na}_2\text{SO}_4$ .  $\text{Na} = 8.78$ .

0.2143       "       "       "       20.8 c.c. nitrogen at  $19^\circ$  and 753 mm.  $\text{N} = 11.05$ .

$\text{C}_{11}\text{H}_{11}\text{NaN}_2\text{O}_4$  requires  $\text{Na} = 8.91$ ;  $\text{N} = 10.85$  per cent.

On adding silver nitrate to the aqueous solution of this substance, a yellowish precipitate of the corresponding silver compound,  $\text{C}_{11}\text{H}_{11}\text{AgN}_2\text{O}_4$ , is thrown down, which dissolves in water with great difficulty.

0.2745 (dried at  $100^\circ$ ) gave 0.0865 Ag.  $\text{Ag} = 31.51$ .

$\text{C}_{11}\text{H}_{11}\text{AgN}_2\text{O}_4$  requires  $\text{Ag} = 31.48$  per cent.

Most characteristic is the copper derivative of ethylic dicyanoglutaconate, which is precipitated in red-brown glistening needles on mixing aqueous solutions of the sodium compound and copper sulphate. It dissolves in boiling water and, on cooling, crystallises unchanged. The air-dried crystals have the composition  $(\text{C}_{11}\text{H}_{11}\text{N}_2\text{O}_4)_2\text{Cu} + 4\text{H}_2\text{O}$ . They slowly lose their water of crystallisation at  $100^\circ$ , and turn pale brown.

0.3190 (air-dried) lost 0.0385 at 100°.  $\text{H}_2\text{O} = 12.06$ .

$(\text{C}_{11}\text{H}_{11}\text{N}_2\text{O}_4)_2\text{Cu} \cdot 4\text{H}_2\text{O}$  requires  $\text{H}_2\text{O} = 11.90$  per cent.

0.2635 (dried at 100°) gave 22.5 c.c. nitrogen at 10° and 766 mm.  $\text{N} = 10.3$ .

0.2800     "     "     "     0.0412  $\text{CuO}$ .  $\text{Cu} = 11.73$ .

$(\text{C}_{11}\text{H}_{11}\text{N}_2\text{O}_4)_2\text{Cu}$  requires  $\text{N} = 10.50$  ;  $\text{Cu} = 11.82$  per cent.

In order to isolate ethylic dicyanoglutaconate, the sodium compound is dissolved in warm water, an excess of hydrochloric acid gradually added to the solution, and the yellow ethylic salt which soon separates is collected and washed with water until the washings are no longer acid. The pale yellow filtrate, after some days, loses its colour and acquires a beautiful blue fluorescence, whilst colourless needles are deposited ; the small amount of the latter precluded us from examining it further.

Ethylic dicyanoglutaconate dissolves readily in hot acetone, and crystallises from it in yellow, glittering plates which melt and decompose at 187—188°. It was found to contain a small quantity of another substance which was not removed by repeated recrystallisation. The following analytical results show that the percentage of carbon in different specimens of the product varies from the theoretical number by one to two per cent.

0.2179 gave 0.4320  $\text{CO}_2$  and 0.1090  $\text{H}_2\text{O}$ .  $\text{C} = 54.07$  ;  $\text{H} = 5.55$ .

0.2012     "     0.4015  $\text{CO}_2$      "     0.0975  $\text{H}_2\text{O}$ .  $\text{C} = 54.42$  ;  $\text{H} = 5.38$ .

0.2073     "     0.4198  $\text{CO}_2$      "     0.1020  $\text{H}_2\text{O}$ .  $\text{C} = 55.22$  ;  $\text{H} = 5.46$ .

0.2258     "     0.4525  $\text{CO}_2$      "     0.1103  $\text{H}_2\text{O}$ .  $\text{C} = 54.65$  ;  $\text{H} = 5.42$ .

0.1980     "     19.5 c.c. nitrogen at 17° and 765 mm.  $\text{N} = 11.50$ .

0.2050     "     20.5     "     "     16°     "     763 mm.  $\text{N} = 11.70$ .

$\text{C}_{11}\text{H}_{12}\text{N}_2\text{O}_4$  requires  $\text{C} = 55.93$  ;  $\text{H} = 5.08$  ;  $\text{N} = 11.86$  per cent.

A similar observation was made by Errera (*loc. cit.*), who was also unable to obtain the ethylic salt in a pure state by crystallising it from alcohol, although he states that he succeeded in removing the impurity by benzene, and that the compound thus purified melts at 178—179°.

The question arose whether ethylic dicyanoglutaconate under the influence of ammonia undergoes a decomposition analogous to that of ethylic dicarboxylglutaconate (Ruhemann and Morrell, *Trans.*, 1891, 59, 743). Experiment, however, showed that such a reaction does not take place either on leaving the ethereal salt in contact with aqueous ammonia at the ordinary temperature or on heating it with the reagent at 100°. The ethereal salt dissolves, and on concentrating the yellow solution, almost colourless, silky needles of the ammonium compound of ethylic dicyanoglutaconate crystallise ; this dissolves fairly easily in cold water, and with the greatest ease on boiling ; it melts and decomposes at 162—163°.

The following analytical data point to the view than this substance, when dried at  $100^{\circ}$ , contains  $\frac{1}{2}\text{H}_2\text{O}$ .

0.2397 (dried at  $100^{\circ}$ ) gave 0.4455  $\text{CO}_2$  and 0.1132  $\text{H}_2\text{O}$ .  $\text{C}=50.71$ ;  $\text{H}=6.17$ .  
 0.2396           ,,           ,, 33.5 c.c. nitrogen at  $22^{\circ}$  and 772 mm.  $\text{N}=16.08$ .  
 0.2267           ,,           ,, 31 c.c.           ,,            $20^{\circ}$    ,, 775 mm.  $\text{N}=15.95$ .  
 $\text{C}_{11}\text{H}_{12}\text{N}_2\text{O}_4, \text{NH}_3 + \frac{1}{2}\text{H}_2\text{O}$  requires  $\text{C}=50.38$ ;  $\text{H}=6.10$ ;  $\text{N}=16.03$  per cent.

On heating the ammonium compound to  $110^{\circ}$ , it turns yellow, and most probably suffers partial dissociation into ammonia and the ethylic salt.

We have, as stated above, undertaken the preparation of ethylic dicyanoglutaconate with a view of ascertaining whether it can readily be transformed into ethylic dihydroxydinicotinate. This change may indeed be effected, and this fact affords an explanation of the formation of the pyridine derivative from the product contained in the mother liquor of ethylic sodiodicarboxyglutaconate.

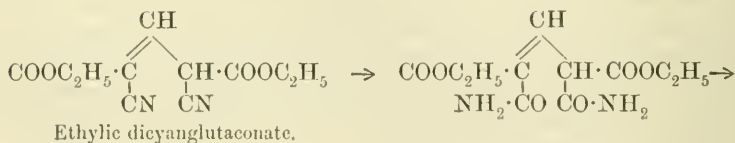
#### *Ethylic Dihydroxydinicotinate.*

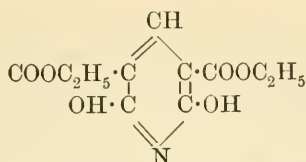
If ethylic dicyanoglutaconate, or the sodium compound of the ethereal salt, is boiled with dilute hydrochloric acid, the substance after a short time enters into solution, and in the course of a few minutes a solid separates, which rapidly increases in quantity. When cold, this is collected, washed, and dried, and then treated with cold concentrated hydrochloric acid, which dissolves most of it; on adding water, a precipitate is thrown down which readily dissolves in chloroform, and crystallises from alcohol in colourless needles. This compound is characterised as ethylic dihydroxydinicotinate by the melting point ( $202^{\circ}$ ), the reddish-violet coloration produced on adding ferric chloride to its alcoholic solution, and by a nitrogen determination.

0.2025 gave 10 c.c. nitrogen at  $20^{\circ}$  and 772 mm.  $\text{N}=5.73$ .

$\text{C}_{11}\text{H}_{13}\text{NO}_6$  requires  $\text{N}=5.49$  per cent.

The formation of ethylic dihydroxydinicotinate is undoubtedly preceded by that of the diamide of ethylic dicarboxyglutaconate, which then loses ammonia and condenses to the pyridine derivative, as illustrated by the following symbols.





Ethylic dihydroxydinicotinate.

On prolonged boiling with hydrochloric acid, ethylic dihydroxydinicotinate decomposes, losing carbon dioxide, and on evaporating the solution on the water bath, the residue gives a reddish-violet coloration with ferric chloride, and strongly reduces silver nitrate and potassium permanganate. The investigation of this compound is not yet complete; there can, however, be no doubt that it is *αα'*-dihydroxypyridine, which could not be isolated from the product of the interaction of ammonia and ethylic glutaconate, on account of the rapidity with which the dihydroxypyridine is oxidised by the oxygen of the air in ammoniacal solution (*see* Ruhemann and Morrell, *Trans.*, 1891, 59, 745).

Ethylic dihydroxydinicotinate not only forms a sodium and an ammonium derivative, but with phenylhydrazine also yields a compound which is thrown down on adding the hydrazine to a warm alcoholic solution of the ethylic salt. It dissolves but sparingly in boiling alcohol, and, on cooling, crystallises in groups of slender, colourless needles which decompose at 198°.

0.2130 gave 0.4365 CO<sub>2</sub> and 0.1112 H<sub>2</sub>O. C = 55.89; H = 5.80.

0.2278 „ 22.5 c.c. nitrogen at 19° and 769 mm. N = 11.49

C<sub>11</sub>H<sub>13</sub>NO<sub>6</sub>·NH<sub>2</sub>·NH·C<sub>6</sub>H<sub>5</sub> requires C = 56.19; H = 5.78; N = 11.57 p. c.

The hydroxyl groups in ethylic dihydroxydinicotinate have the same relative position in the pyridine ring as in citrazinamide; the latter, as shown some time ago (Ruhemann, *Ber.*, 1887, 20, 3369), may be transformed into trichlorocitrazinamide and the corresponding bromo-derivative, by the action of chlorine or bromine on the solution of the amide in hydrochloric acid. It seemed to be of some interest to subject ethylic dihydroxydinicotinate to a similar treatment with the view of arriving at analogous halogen derivatives. The ethylic salt, as has been stated before (Ruhemann and Sedgwick, *Ber.*, 1895, 28, 825), and as mentioned in this paper, has feeble acid properties; it dissolves in concentrated hydrochloric acid, but the hydrochloride thus formed dissociates on adding water. This behaviour of ethylic dihydroxydinicotinate has been made use of for its purification. On adding bromine to the solution of the ethylic salt in hydrochloric acid, an unstable additive product is formed (Ruhemann and Sedgwick, *loc. cit.*); chlorine however, we find, behaves differently.

*Ethylic Dihydroxydichloronicotinate.*

On saturating the solution of ethylic dihydroxydinicotinate in concentrated hydrochloric acid with chlorine, a viscid mass separates and adheres to the sides of the vessel; this is washed, dissolved in dilute potash, and the solution acidified with hydrochloric acid, when a white precipitate is obtained which is sparingly soluble in boiling alcohol, and on cooling crystallises in colourless, shiny plates. These begin to darken at about  $238^{\circ}$ , and are completely decomposed at  $248^{\circ}$ ; ferric chloride gives a reddish-violet coloration with their alcoholic solution.

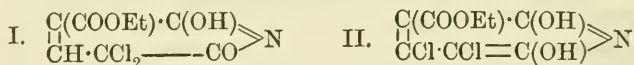
On analysis, numbers were obtained corresponding with the formula  $C_8H_7NO_4Cl_2$ .

0.2090 gave 0.2930  $CO_2$  and 0.0528  $H_2O$ .  $C = 38.23$ ;  $H = 2.80$ .

0.2318 „ 0.2636  $AgCl$ .  $Cl = 28.14$ .

$C_8H_7NO_4Cl_2$  requires  $C = 38.10$ ;  $H = 2.78$ ;  $Cl = 28.17$  per cent.

The mode of formation of the compound and the analytical results indicate that it is ethylic dichlorodihydroxynicotinate; its constitution may, *a priori*, be expressed by one of the formulæ.



The first formula, I, would correspond with the structure of trichlorocitrazinamide and to that of the dichloro-derivative formed from methyl dihydroxypyridine (Ruhemann, *Ber.*, 1894, **27**, 1271), but the stability of ethylic dichlorodihydroxynicotinate compared with that of the others would indicate that the formula II has to be assigned to it. This formula is, moreover, supported by the behaviour of the substance towards phenylhydrazine. Whilst the former chloro-derivatives, on treatment with the base, are transformed into phenylhydrazones, with removal of halogen, the latter yields merely an additive product. This readily dissolves in alcohol, and on treatment with dilute hydrochloric acid the chloro-derivative is precipitated unchanged.

In conclusion, we express our best thanks to Mr. O. Reinherz, of Trinity College, for help afforded us in the course of this work.

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XXIX.—*The Action of Alkyl Iodides on Silver Malate and on Silver Lactate.*

By THOMAS PURDIE, F.R.S., and G. DRUCE LANDER, B.Sc.

THE silver salts of organic acids react, as a rule, very readily and completely with the lower alkyl iodides, and as the chemical change usually follows a perfectly normal course, it affords, as is well known, one of the most trustworthy processes for the preparation of ethereal salts, furnishing a pure product and a satisfactory yield in many cases where the commoner processes of etherification cannot be employed. The method obviously recommends itself for the preparation of the ethereal salts of optically active acids which are liable to have their activity impaired by the action of mineral acids; for this reason, it was employed in the preparation of the active ethereal alkyloxy-succinates (Trans., 1895, 67, 970), and it gave satisfactory results. In applying the method, however, to hydroxy-acids, we find that the reaction does not proceed entirely in the normal direction, and that it cannot be relied on to produce the ethereal salts of such acids in a state of purity.

J. Wallace Walker (Trans., 1895, 67, 916) prepared ethereal lactates from the silver salt and found them to be more active than specimens prepared by other investigators by the commoner methods. This result suggested a research on the optical activity of ethereal malates and lactates prepared by different methods (Purdie and Williamson, Trans., 1896, 69, 818), which showed that in general the ethereal salts obtained by the action of primary iodides on the silver salts did, in fact, exhibit a considerably higher activity than those prepared with the aid of hydrochloric or sulphuric acid, the difference amounting in some cases to about 20 per cent. of the total activity. The reaction in these cases appeared, nevertheless, to run its normal course; the results of analysis, the nearly constant boiling points of the products, the yield obtained, and the comparative constancy of the activity of different preparations seemed to preclude the idea that the ethereal salts could be contaminated with substances of higher activity. The obvious alternative explanation, that the lower activity of the ethereal salts made by the commoner methods might be due to racemisation, was not supported by experiment, as racemic compounds could not be detected in the products of hydrolysis in such quantity as would account for the defect in activity. No explanation of the apparent anomaly could be given. In attempting to prepare isopropyl malate (*loc. cit.*), it was found that the action of isopropyl iodide on silver malate was quite abnormal. The yield of ethereal salt obtained was very small, the activity of different preparations varied considerably, and was nearly two and a half times as great as that of normal propyl malate, an

observation which is quite at variance with what is known of the relative influence of the two propyl groups on optical activity. The results of analysis and experiments on the hydrolysis of the ethereal salt led the authors to conclude that the product was a mixture of isopropyl malate with some more carbonaceous and much more optically active substance. The object of the present investigation was to ascertain the cause of the anomalous results referred to. We find that the high activity of the product of the action of isopropyl iodide on silver malate is due to the presence in it of a considerable amount, more than 20 per cent., of isopropyl isopropoxy- or propoxy-succinate, the propyl group of the iodide having replaced, not only the silver of the salt, but also to some extent the hydrogen of the alcoholic hydroxyl, and that an analogous reaction occurs between isopropyl iodide and silver lactate. We have succeeded also in establishing the fact that ethyl malate and ethyl lactate, made by the method referred to, notwithstanding the evidence for their purity, mentioned above, are in reality contaminated, although to a much smaller extent, with more highly carbonaceous and more active substances, which, although we could not isolate them in a state of purity, are without doubt the corresponding ethoxy-compounds.

*Action of Isopropyl Iodide on Silver Malate.*

In carrying out the reaction, the method pursued was as follows. The finely powdered dry silver malate was added, a small portion at a time, to excess of isopropyl iodide, the temperature being allowed to rise. The mixture having been heated for an hour on a water bath, was diluted with dry ether and filtered; the filtrate, being extremely acid, was allowed to stand over potassium carbonate, again filtered, and after removal of the ether distilled under reduced pressure. After the iodide had distilled off, the liquid boiled at a nearly constant temperature. We employed 360 grams of silver malate and 600 grams of iodide, and obtained after two distillations 68 grams of a product having the boiling point  $163\text{--}165^\circ$  under a pressure of 60 mm. A small quantity of the substance was accidentally lost during distillation, but making allowance for this, the yield amounted to only about a half of that obtained (*loc. cit.*) with primary propyl iodide. The observed rotation of the liquid was  $\alpha = -65.92^\circ$  in a 200 mm. tube at  $20^\circ$ , the rotations found in the previous preparations on a smaller scale being  $-69.80^\circ$  and  $-61.95^\circ$ ; that of *n*-propyl malate made by the same method is  $-29.6^\circ$ . Normal propyl and isopropyl malate, prepared by Walden by Anschütz's method (*Zeit. physikal. Chem.*, 1895, 17, 248) showed under similar conditions the rotations  $-24.96^\circ$  and  $-23.06^\circ$  respectively.

In order to isolate the more active constituent, 66 grams of the mixture were shaken in the cold with a 10 per cent. aqueous solution of potassium hydroxide and left in contact with the alkaline solution for 24 hours, previous experiments having shown that by this treatment the less active substance was first hydrolysed. The residual oil, after being washed with water and separated from the latter by the addition of some ether, amounted to 15 grams. It was found that the removal of the less active constituent had raised the rotation from  $\alpha = -32.9^\circ$  to  $-54.95^\circ$  in a 100 mm. tube. On being distilled under a pressure of about 25 mm., nearly all the liquid passed over at  $148^\circ$ . The analysis of the liquid gave results agreeing with the formula of propylic propoxysuccinate.

0.0980 gave 0.2155  $\text{CO}_2$  and 0.0825  $\text{H}_2\text{O}$ .  $\text{C} = 59.97$ ;  $\text{H} = 9.35$ .

0.1670 „ 0.3660  $\text{CO}_2$  „ 0.1385  $\text{H}_2\text{O}$ .  $\text{C} = 59.77$ ;  $\text{H} = 9.21$ .

$\text{C}_{13}\text{H}_{24}\text{O}_5$  requires  $\text{C} = 60.00$ ;  $\text{H} = 9.23$  per cent.

A determination of the specific rotation of the substance gave the following result:  $t = 18^\circ$ ,  $l = 1$ ,  $\alpha = -57.08$ ,  $d_{17.5/4^\circ} = 0.9762$ ,  $[\alpha]_D = -58.47^\circ$ . Its activity far exceeds that of normal and isopropylic malates, the specific rotations of which are respectively only  $-11.6^\circ$  and  $-10.41^\circ$  (Walden, *loc. cit.*; Anschütz, *Zeit. physikal. Chem.*, 1895, 16, 495).

The ethereal salt, although not attacked by 10 per cent. aqueous potassium hydroxide in the cold, was readily hydrolysed when heated on the water bath with aqueous alkali to which enough alcohol had been added to bring the oil into solution; a small portion of it was therefore hydrolysed in this manner. On adding silver nitrate to the neutralised solution, a silver salt was obtained as a gelatinous, white precipitate, differing essentially in appearance from silver malate, which is a crystalline powder; it was much more difficult to wash than the latter, and apparently more soluble in water. Unlike silver malate, it turned rapidly brown when dried at  $100^\circ$ , and even at the ordinary temperature in a vacuum became dark coloured. Estimations of silver, therefore, did not give satisfactory results; the numbers obtained with the salt dried in a vacuum and at  $100^\circ$  were 59.30 and 60.81 per cent. respectively, the calculated percentages for silver propoxysuccinate and malate being 55.38 and 62.07.

As it seemed possible that potassium hydroxide might have decomposed the acid, the rest of the ethereal salt was hydrolysed by heating with an aqueous alcoholic solution of barium hydroxide. After removing the excess of the latter with carbonic anhydride and evaporating the solution to a small bulk, the barium salt separated as a white, indistinctly crystalline powder of pearly lustre; this was readily soluble in water, leaving, however, a small residue of a highly in-

soluble salt, probably barium malate, which was removed by filtration. As trustworthy determinations of water of crystallisation in the barium alkyloxysuccinates are difficult to obtain owing to their hygroscopic character, some of the salt was dried for analysis at 130—140°. The results found on combustion were as follows. I. C=26.19; H=3.22; Ba=44.19. II. C=26.29, H=3.26, Ba=44.41; the calculated percentages for barium propoxysuccinate are C=27.01; H=3.22; Ba=44.05. Estimations of barium gave 43.70 and 43.96 per cent. The low results for carbon shown in the combustions may possibly be due to the difficulty of drying the salt completely without its undergoing slight decomposition.

The specific rotation of the salt was observed in solutions of different strengths, the concentration of the initial solutions, from which others were made by dilution, being found by evaporating a measured volume and weighing the residue dried at 130—140°.

- (1)  $t = 19^\circ$ ,  $l = 4$ ,  $c = 12.95$ ,  $a = -4.11^\circ$ ,  $[\alpha]_D = -7.93^\circ$ .
- (2)  $t = 19^\circ$ ,  $l = 4$ ,  $c = 6.475$ ,  $a = -2.72^\circ$ ,  $[\alpha]_D = -10.50^\circ$ .
- (3)  $t = 20^\circ$ ,  $l = 4$ ,  $c = 6.170$ ,  $a = -2.72^\circ$ ,  $[\alpha]_D = -11.02^\circ$ .
- (4)  $t = 20^\circ$ ,  $l = 4$ ,  $c = 3.085$ ,  $a = -1.50^\circ$ ,  $[\alpha]_D = -12.16^\circ$ .

The activity of this salt differs widely from that of barium malate, which, according to Schneider (*Annalen*, 1881, 207, 277), has the specific rotation  $+4.69^\circ$  when  $c = 5.19$ .

The acid was obtained from the solution of the barium salt by adding rather less than the calculated quantity of sulphuric acid. The solution having been filtered and the filtrate evaporated to dryness, the acid was extracted from the residue with ether, and on evaporating the ether it was left as an oil which quickly solidified to a crystalline mass. It was, however, very deliquescent, and did not show a sharp melting point. Observations of the activity of its aqueous solution are given below; the concentrations were found in the case of the first three determinations by titrating the initial solution with standard alkali and diluting this to known volumes, and in the case of the fourth by weighing the acid directly.

- (1)  $t = 18^\circ$ ,  $l = 4$ ,  $c = 10.0036$ ,  $a = -14.51^\circ$ ,  $[\alpha]_D = -36.26^\circ$ .
- (2)  $t = 16^\circ$ ,  $l = 4$ ,  $c = 5.0018$ ,  $a = -7.21^\circ$ ,  $[\alpha]_D = -36.04^\circ$ .
- (3)  $t = 16^\circ$ ,  $l = 4$ ,  $c = 2.5009$ ,  $a = -3.66^\circ$ ,  $[\alpha]_D = -36.59^\circ$ .
- (4)  $t = 18^\circ$ ,  $l = 4$ ,  $c = 3.3583$ ,  $a = -4.74^\circ$ ,  $[\alpha]_D = -35.29^\circ$ .

The calcium salt, prepared by neutralising the acid with calcium carbonate, was only sparingly soluble in cold water, and still less so in hot water; on slightly warming a cold saturated solution, it became rapidly turbid from the separation of the salt in the form of fine scales, which, on cooling, went again into solution. The salt, dried at 110°,



was found to contain 18.71 per cent. of calcium, and combustion gave the following results.

Found I. C = 38.60; H = 4.48; Ca = 18.30.

„ II. C = 38.82; H = 4.65; Ca = 18.74.

Calculated for calcium propoxysuccinate,  $C_7H_{10}O_5Ca$ , C = 39.25; H = 4.67; Ca = 18.69 per cent.

To determine the specific rotation, a solution was made by shaking the salt with cold water, and its concentration was found by evaporating an aliquot portion to dryness and weighing the dried residue; the following result was obtained.

$$t = 18^\circ, l = 4, c = 1.635, \alpha = -1.28^\circ, [\alpha]_D = -19.57^\circ.$$

A solution of the potassium hydrogen salt, prepared by exactly neutralising a measured volume of the solution of the acid with standard potassium hydroxide, adding an equal quantity of acid, and making the liquid up to a definite volume, gave the following specific rotation.

$$t = 18^\circ, l = 4, c = 1.6992, \alpha = -2.16^\circ, [\alpha]_D = -31.78^\circ.$$

A solution of the normal potassium salt was also prepared by exactly neutralising a solution of the acid with standard potassium hydroxide and making up the liquid to a known volume. The specific rotation was as follows.

$$t = 16^\circ, l = 4, c = 3.9820, \alpha = -3.03^\circ, [\alpha]_D = -19.02^\circ.$$

A portion of the solution was evaporated and an estimation of potassium made in the salt dried at  $100^\circ$ . Found, K = 30.85; calculated for  $C_7H_{10}O_5K_2$ , 31.01 per cent.

The optical observations and the analyses which have been quoted prove that the abnormally high activity of the product of the action of isopropyl iodide on silver malate is due to the unexpected formation of a considerable amount of isopropyl propoxy- or isopropoxy-succinate. This conclusion is borne out by a comparison of the activity of the substances described with that of the corresponding derivatives of active normal propoxysuccinic acid obtained by the resolution of the inactive acid which was prepared by the addition of normal propyl alcohol to maleic anhydride or propyl fumarate (Trans., 1895, 67, 949). The ethereal salts of this acid have not been prepared, but judging from the active methoxy- and ethoxy-succinates, the observed activity of the compound we have isolated is such as a propyl propoxysuccinate would be expected to exhibit. The specific rotation of propyl methoxysuccinate is  $45.21^\circ$ , that of the corresponding ethoxysuccinate  $51.25^\circ$  (Trans., 1895, 67, 979); assuming that the rise of activity is nearly constant in ascending the series, the specific rotation of propyl



*n*-propoxysuccinate should be about  $57^{\circ}$ , and that of the isopropyl compound should not differ much from this value. The specific rotation of our compound is  $58.47^{\circ}$ . The two acids show nearly the same specific rotation in aqueous solution, and the activity in both cases alters but slightly on dilution. Taking the mean of the observations at different concentrations, the specific rotation of *n*-propoxysuccinic acid from fumaric acid is  $36.23^{\circ}$ , that of the compound formed from malic acid, as described above,  $36.04^{\circ}$ . The rotations of the potassium hydrogen salts in dilute solution are also similar, namely,  $32.30^{\circ}$  and  $31.78^{\circ}$  respectively. In the case, however, of the normal potassium salt, and of the calcium and barium salts whose specific rotation alters largely with dilution, the salts from malic acid show a somewhat higher activity than the salts from the other source. Thus, the normal potassium salts have, in 3 to 4 per cent. solution, the specific rotations  $19.02^{\circ}$  and  $17.26^{\circ}$  respectively; the calcium salts, resembling each other in their sparing solubility in water, and in their greater solubility in cold than in hot water, show in dilute solution the specific rotations  $19.57^{\circ}$  and  $14.18^{\circ}$  respectively. The barium salt of our acid shows the same rapid rise of activity with dilution which is exhibited by the barium alkyloxysuccinates in general (Trans., 1893, 63, 239). The specific rotations of the barium propoxysuccinates from the two sources for about equal concentrations are  $12.16^{\circ}$  and  $10^{\circ}$  respectively.

Our experiments afford no conclusive evidence as to whether the acid under investigation is a normal propoxy- or an isopropoxy-derivative of succinic acid. The similarity in activity of the acids and of the acid potassium salts favours the former view; on the other hand, the difference exhibited by the other three salts mentioned are such as might be expected if the acids were isomeric. It may be mentioned that, in the case of the sparingly soluble calcium salts, where the difference is greatest, the solutions examined were so dilute that the observations of activity may be affected with a considerable error.

With regard to the composition of the mixture of ethereal salts resulting from the interaction of isopropyl iodide and silver malate, the chief constituent is, no doubt, the normal product, namely, isopropyl malate. This was confirmed by neutralising the alkaline solution used in effecting the partial hydrolysis, and adding silver nitrate, when silver malate was precipitated; the salt, dried at  $100^{\circ}$ , was found to contain 62.14 per cent. of silver, the calculated percentage being 62.07. The quantity of malic acid in this solution was estimated approximately by weighing the silver malate precipitated from an aliquot part of it. The quantity of isopropyl malate, corresponding to the malic acid found, would amount to about 80 per cent. of the weight of the mixture of ethereal salts, from which it follows that the propoxysuccinate constituted about 20 per cent. of the

mixture; the quantity actually isolated by the partial hydrolysis was 23 per cent. It should be mentioned, however, that from the optical observations it would appear that either the quantity of this substance separated was much less than that actually formed, a considerable part of it having undergone hydrolysis even in the cold potassium hydroxide solution, or else there was some other substance more active than isopropyl malate in the mixture. If the product consisted only of isopropyl malate and isopropyl propoxysuccinate, the quantity of the latter, calculated from the rotations of the separate constituents\* and of the mixture, should have amounted to more than 40 per cent. of the whole.

*Action of Ethylic Iodide on Silver Malate.*

As already stated, the ethereal malates from the action of primary iodides on silver malate were found to be more active than the corresponding substances prepared from malic acid and alcohol with the aid of mineral acids. The differences of activity, however, in these cases are small as compared with that observed with isopropyl malate; the specific rotations found for ethyl malate, for example, from the two different sources were  $-12.4^{\circ}$  and  $-10.3^{\circ}$ . Besides this, in the case of the malates of primary alcoholic radicles, neither boiling point nor analysis indicated the presence of foreign substances, so that it was only after ascertaining the cause of the abnormal activity of the product obtained from isopropyl iodide that it occurred to us that the malates made from primary iodides probably also owed their higher activity to the formation of alkylloxysuccinic acids. Five per cent. of ethyl ethoxysuccinate would suffice to account for the difference in activity observed in the case of ethyl malate. The substances differ so little in percentage composition that analysis would not betray the contamination, and the boiling points also are so much alike that fractional distillation of small quantities of material might readily fail to detect it.

We accordingly prepared ethyl malate in the manner previously described (*loc. cit.*), but on a larger scale. We employed 454 grams of silver malate and 868 grams of ethyl iodide, and obtained 200 grams of ethereal salt, boiling at  $130-135^{\circ}$  under a pressure of 15 mm. and the rotation  $\alpha = -13.93^{\circ}$  in a 100 mm. tube at  $12^{\circ}$ ; the rotations observed in previous preparations were  $-14.06^{\circ}$  and  $-14.30^{\circ}$ . On being redistilled under reduced pressure, the whole liquid boiled within a range of  $4^{\circ}$ , but the activity of the first fraction collected, 86 grams, was found to have risen to  $-14.8^{\circ}$ , and that of the last to have decreased to  $-12.6^{\circ}$ . On further repeated distillation, the activity of the fractions

\* The activity of isopropyl malate has been determined by Walden (*loc. cit.*).

of lower boiling point increased continuously, whilst that of the higher boiling fractions decreased, but to a smaller extent. Owing to slight variations of pressure, it was not possible to observe the exact boiling points of the various fractions under identical conditions, but those of the extreme fractions did not differ by more than  $3^{\circ}$  or  $4^{\circ}$ . Finally, after prolonged fractionation, 17 grams were collected, having the rotation  $\alpha = -17.05$ , whilst much the larger part of the liquid had accumulated in the fractions of higher boiling point, the rotation of which had decreased to  $-12.2^{\circ}$ . The maximum rotation had evidently not been nearly reached, but the quantity of material did not admit of the fractionation being carried further; the very slow decrease of activity in the case of the fractions of higher boiling point, on the other hand, indicated that the minimum rotation had been much more nearly attained, the minimum being evidently that of ethylic malate as prepared by the usual methods, namely,  $\alpha = -11.7^{\circ}$ . That the substances of higher and lower activity were not produced by any chemical change caused by the repeated distillation was proved by an analysis of the latter, which showed that it still retained the composition of ethylic malate. We found on combustion  $C = 50.45$ ;  $H = 7.41$ , the calculated numbers being 50.53 and 7.37 per cent.

The results of the fractional distillation show that the product of the action of ethylic iodide on silver malate is mainly ethylic malate, but that the ethereal salt is contaminated with a small quantity of a much more active substance, probably ethylic ethoxysuccinate. It seemed that it would be impossible to isolate the ethoxysuccinic acid without repeating the experiment on a still larger scale; with the view, however, of finding corroborative evidence of the presence of this acid, we examined the products of hydrolysis of the more active fractions of the ethereal salt. A brief account of the results of this examination may be given.

One of the more active fractions was partially hydrolysed by treatment with aqueous caustic alkali in the cold, which raised the rotation of the unhydrolysed part considerably. A sparingly soluble calcium salt, prepared from this more active portion by hydrolysing it with calcium hydroxide, was found, on combustion, to have a percentage composition intermediate between that of calcium malate and calcium ethoxysuccinate. The fraction of ethereal salt having the rotation  $\alpha = -17.05^{\circ}$  was similarly subjected to partial hydrolysis, which raised the rotation of the residual oil only to  $-20^{\circ}$ ; this method of separating the constituents of the mixture was not so effective as it had proved in the case of isopropyl malate. The hydrolysed part contained chiefly malic acid; the calcium salt prepared from it, after drying at  $140^{\circ}$ , contained 21.30 per cent. of calcium, the percentage for monhydrated calcium malate being 21.05. The residual un-

hydrolysed part gave, on hydrolysis with barium hydroxide, two barium salts, one sparingly soluble, the other readily soluble in water. The insoluble salt, which was precipitated as a granular powder on boiling the solution, was approximately pure barium malate. It contained, when dried at 120—130°, 50·51 per cent. of barium, the calculated percentage being 50·93. The soluble salt, consisting of crystalline scales, when dried under similar conditions, contained 47·88 per cent. of barium, a result intermediate between the calculated percentages of malate and ethoxysuccinate, but nearer that of the latter, which is 46·13. Polarimetric observations were also in agreement with the supposition that the soluble salt was a mixture of the salts of ordinary malic acid and *l*-ethoxysuccinic acid. The activity of both barium salts is known to vary much with concentration, the change with dilution being in both cases in the lævo-direction, but for similar concentration the ethoxysuccinate is much less dextrorotatory or much more lævorotatory than the malate. The specific rotations found were + 6·85° for  $c = 15\cdot92$  and + 3·02° for  $c = 7\cdot96$ , results intermediate between those which the pure salts would have given under similar conditions. (*Annalen*, 1881, 207, 277; *Trans.*, 1893, 63, 235). We prepared a larger quantity of the mixed barium salts from some of the more active fractions of the ethereal salt, and tried to remove the malate by repeated boiling and evaporation, by which treatment it separates in the anhydrous insoluble form, but the separation was only partial; analysis and polarimetric examination of the soluble salt showed that the malate had been further eliminated, but that much was still present. Attempts to purify the ethoxysuccinate by conversion into the lead and the calcium salts also failed.

*Action of Normal Butylic Iodide on Silver Malate.*

Anschütz and Reitter have shown that normal butylic malate, prepared by the hydrochloric acid method, has the specific rotation  $-10\cdot722^\circ$  (*Zeit. physikal. Chem.*, 1895, 16, 495); the product of the action of normal butylic iodide on silver malate has the specific rotation  $-12\cdot20^\circ$ . Having a small quantity, 12 grams, of the latter substance, we examined the product of its hydrolysis to ascertain whether it contained, besides malic acid, the more lævorotatory butoxysuccinic acid. On boiling the solution of the barium salt, obtained by hydrolysing the ethereal salt with barium hydroxide, a large quantity of barium malate was precipitated, but there remained some barium salt readily soluble in water which was not rendered insoluble on prolonged boiling of the solution. An estimation of barium in this gave a result midway between that of malate and butoxysuccinate, and a 6 per cent. solution showed only a slight dextrorotation. At this concentration,



barium malate is more dextrorotatory, and barium butoxysuccinate is lævorotatory. The quantity of material was too small to attempt a separation.

*Action of Alkyl Iodides on Silver Lactate.*

It has been shown (*loc. cit.*) that ethylic lactate prepared from the silver salt exhibits a higher activity than when prepared by other methods. Klimenko and J. Wallace Walker, using the former method, found the specific rotation to be  $14.19^\circ$  and  $14.52^\circ$  respectively; Purdie and Williamson, by the same method, obtained a somewhat lower result,  $13.46^\circ$ , but still notably higher than the activity found in the case of the ethereal salt prepared with the aid of sulphuric acid, the specific rotation of which was only  $10.33^\circ$ . Examination of the active zinc lactate obtained from the latter ethereal salt proved that its lower activity was not due to racemisation. In view of what has been stated above with regard to the action of isopropyl iodide on silver malate, it seemed probable that the excess of activity exhibited by ethylic lactate prepared from silver lactate was to be attributed to the production of a small quantity of ethylic ethoxypropionate. We have been engaged recently in resolving inactive alkyloxypropionic acids into their active components, and find that these compounds possess a very high degree of activity as compared with lactic acid, so that the presence of a small proportion of ethylic ethoxypropionate would suffice to account for the excess of activity referred to. As the two ethereal salts have practically the same boiling point, the ethoxypropionate would not be removed by fractional distillation, and the presence of such a small quantity of the substance as would suffice to raise the rotation to the degree mentioned would not be readily detected by analysis. Our immediate object in the following experiments being only to ascertain if alkyloxypropionates are produced simultaneously with lactates when alkyl iodides act on silver lactate, inactive lactic acid was employed.

Ethylic lactate was prepared from the silver salt in the manner previously described. From 173 grams of lactate and 290 grams of ethylic iodide, we obtained 57 grams of ethereal salt having the boiling point  $151-154^\circ$  under atmospheric pressure; the small yield, amounting to only 55 per cent. of the calculated quantity, indicated that the reaction had not proceeded entirely in the normal manner. The distinctive properties of the zinc salts of ethoxypropionic acid and lactic acid presented a method of detecting the former in the presence of a large quantity of the latter, or, possibly, even of separating it in the pure state, zinc ethoxypropionate being a gum soluble in alcohol, zinc lactate, as is well known, a crystalline salt nearly insoluble in that liquid. The ethereal salt, accordingly, was converted into barium salt by boiling



with solution of barium hydroxide and removal of the excess of the latter with carbonic anhydride. The acid was obtained from the barium salt by adding to its solution rather less than the calculated quantity of sulphuric acid, evaporating the filtered liquid, and extracting the residue with ether. Finally, the acid was converted into zinc salt by means of zinc carbonate, and the solution having been evaporated, the dried residue was treated with absolute alcohol. The great bulk of the salt was left undissolved, and on evaporating the filtered liquid a zinc salt was left in the form of a gum. The separation, however, was evidently not complete, as some zinc lactate crystallised from the gum on standing. Zinc lactate, in fact, dissolved in the alcoholic solution of the uncrystallisable zinc salt to a much greater extent than in pure alcohol, and although a considerable amount of the lactate was removed by repeated evaporation and treatment with alcohol, and also by adding alcohol to the aqueous solution, the separation was not complete. The salt, dried at  $150^{\circ}$ , at which temperature it showed no signs of decomposition, was found to contain 23.38 per cent. of zinc, the calculated percentages for zinc lactate and ethoxypropionate being 26.87 and 21.84 respectively. A combustion of a crystalline calcium salt which was made from the uncrystallisable zinc salt gave results for carbon, hydrogen, and calcium intermediate between the calculated numbers for lactate and ethoxypropionate. From 57 grams of ethereal salt, we obtained about 2 grams of the uncrystallisable zinc salt.

To ascertain whether ethylic lactate made by other methods gave similar results, we prepared the compound from inactive zinc lactate, alcohol, and sulphuric acid. The same weight of this ethereal salt as had been used in the experiments just described was converted into zinc salt under exactly the same conditions; and as much as possible was separated by crystallisation from the aqueous solution in order that the uncrystallisable salt, if there were any present, might be more certain of detection. The crystallised salt was pure zinc lactate, being found on analysis to contain 18.06 per cent. of water of crystallisation and 26.89 per cent. of zinc calculated on the anhydrous salt, the calculated numbers being 18.16 and 26.87. The residue left on evaporating the solution to dryness showed no sign of gum, and the alcoholic extract of it, when evaporated to dryness, left a small quantity of zinc lactate with only a trace of viscid matter. In the preparation of ethylic lactate from zinc lactate, just mentioned, a small yield of ethereal salt was obtained. In order to satisfy ourselves that the unetherified acid contained no ethoxypropionic acid, the organic potassium salt, which had been formed on the addition of potassium carbonate to the crude product, was separated from the inorganic salts by alcohol, converted into acid, and then into zinc salt. This salt was crystalline, and proved on analysis to be pure zinc lactate. We could not detect

any ethoxypropionic acid either in the etherified or unetherified acid.

We conclude that ethylic lactate made from silver lactate is contaminated with a small proportion of an ethereal salt of an acid containing more carbon than lactic acid, which, judging from what follows below, is doubtless ethoxypropionic acid, and that it is the presence of this substance which raises the activity of active ethylic lactate made by the method in question. On the other hand, ethylic lactate made by the sulphuric acid method does not contain this impurity, or, if at all, only in very minute quantity.

Our experiments with silver malate having shown that isopropyllic iodide gives a much larger proportion of the alkyloxy-compound than primary iodides, it seemed likely that the same would hold good for silver lactate. We found that this was the case, and that the salts of isopropoxypropionic acid could consequently be prepared from the product of the reaction without much difficulty.

Isopropyllic iodide was found to act readily on silver lactate. The product was strongly acid; having been diluted with ether, it was accordingly neutralised with dry potassium carbonate, which caused the separation of a yellowish, gummy, potassium salt. The filtered liquid was distilled fractionally under atmospheric pressure, and after several distillations much the greater part boiled at 155—161°. The yield of ethereal salt was very small, as in the case of the malate; from 235 grams of silver lactate and 358 grams of isopropyllic iodide we obtained 40 grams boiling at the temperature mentioned, that is to say, only about 25 per cent. of the calculated yield. Isopropyllic lactate, prepared by heating the acid and alcohol, boils, according to Silva (*Bull. Soc. Chim.*, [iii], 17, 97) at 166—168°, and isopropyllic isopropoxypropionate, which was prepared by Silva, by acting on the lactate with sodium and isopropyllic iodide, but was not obtained pure, is stated to have a boiling point a little above that of isopropyllic lactate.

As it was impossible to separate the ethereal salts by fractional distillation, the method of partial hydrolysis which had proved successful in the case of the malate was also employed here. Twenty grams of the ethereal salt (b. p. 155—161°) were shaken with excess of 10 per cent. cold potassium hydroxide solution, and the unaltered oil was separated and washed with water. The alkaline solution, on being acidified with sulphuric acid and extracted with ether, gave lactic acid, as was proved by an analysis of the crystalline zinc salt obtained from it; we found  $H_2O = 18.31$ ,  $Zn = 26.72$ . By boiling the unhydrolysed oil with an aqueous alcoholic solution of barium hydroxide and removal of the excess of the latter with carbonic anhydride, we obtained a barium salt in the form of a gum; this, when dried at 140°, was found to contain 34.33 per cent. of barium, the calculated percentage for

the propoxypropionate being 34.08. The acid, which was obtained from the barium salt by decomposing it with the calculated quantity of sulphuric acid and extracting with ether, was a liquid. The silver salt, prepared from this acid by neutralising it with silver carbonate, crystallised from the cooled aqueous solution as a felted mass of fine needles, not very soluble, and darkening on heating with water. An estimation of silver in the salt dried at  $100^{\circ}$  gave  $\text{Ag} = 45.32$  per cent., and by combustion we found  $\text{C} = 29.41$ ,  $\text{H} = 4.57$ ,  $\text{Ag} = 45.35$ ;  $\text{C}_6\text{H}_{11}\text{O}_3\text{Ag}$  requires  $\text{C} = 30.12$ ,  $\text{H} = 4.60$ ,  $\text{Ag} = 45.19$ . The low result for carbon was probably due to the salt having undergone slight decomposition; an analysis of another, purer, preparation is given below.

Another portion of the residual oil which was unhydrolysable in cold aqueous caustic alkali was hydrolysed by heating with aqueous alcoholic sodium hydroxide, and the acid obtained in the same manner as from the barium salt above mentioned. The zinc salt made from the acid, which was a gum, like the corresponding ethoxypropionate, was converted with calcium hydrate into the calcium salt, which crystallised from a concentrated aqueous solution in small needles containing  $2\text{H}_2\text{O}$ . Found, loss of weight at  $115^{\circ} = 10.58$ ;  $\text{Ca}$  in anhydrous salt =  $13.31$  per cent. Calculated for calcium propoxypropionate,  $2\text{H}_2\text{O} = 10.65$ ;  $\text{Ca} = 13.24$ .

As already stated, the crude product of the action of isopropyl iodide on silver lactate contained much free acid. This acid was found to consist chiefly of lactic acid, mixed, however, with a considerable proportion of propoxypropionic acid. The potassium salt, formed on adding potassium carbonate, was separated from the excess of the latter by boiling alcohol, in which it was soluble; it was a gum which showed no signs of crystallisation. The acid was obtained from it by acidification with sulphuric acid and extraction with ether. It gave a crystalline zinc salt which analysis showed to be pure zinc lactate, and also an uncrystallisable zinc propoxypropionate which was separated from the lactate by taking advantage of its solubility in alcohol. The calcium salt, procured from the gummy zinc salt, crystallised readily in needles, and was found on analysis to have the same composition as the calcium propoxypropionate, an analysis of which is quoted above. The acid, recovered from the calcium salt by acidification with sulphuric acid and extraction with ether, was converted into silver salt, which was now found to be nearly pure, as is shown by the following analysis.

0.2860 gave 0.3115  $\text{CO}_2$ , 0.1175  $\text{H}_2\text{O}$  and 0.1300  $\text{Ag}$ .  $\text{C} = 29.70$ ;  $\text{H} = 4.56$ ;  $\text{Ag} = 45.45$ .

$\text{C}_6\text{H}_{11}\text{O}_3\text{Ag}$  requires  $\text{C} = 30.12$ ;  $\text{H} = 4.60$ ;  $\text{Ag} = 45.19$  per cent.

Our experiments show that the high activity of ethereal malates

and lactates prepared from the silver salts is due to their being contaminated with the salts of the much more highly active alkyloxy-succinic and alkyloxypropionic acids. The quantity of the latter produced may amount, when isopropyl iodide is used, to 20—40 per cent. of the whole product; with primary iodides, on the other hand, the quantity probably does not exceed 5 per cent.

The late J. W. Rodger and J. S. S. Brame (Trans., 1898, '73, 301) found that the ethereal tartrates from silver tartrate have a very abnormally high rotation. Having received Mr. Brame's permission, we are investigating this reaction, and we have already obtained some evidence that the abnormal activity is due to the production of dialkyloxysuccinates.

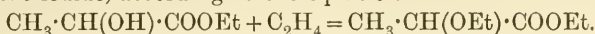
The silver salts of other hydroxy-acids will probably be found to react similarly with alkyl iodides, and this method of preparing ethereal salts, at all events under the conditions observed by us, cannot therefore be used with safety in the case of these acids. The observation was made previously (*loc. cit.*) that whilst the ethereal malates and lactates differed in activity according to their method of preparation, the acidyl derivatives prepared from them had nearly the same rotation; the explanation no doubt is that, owing to the difference of the boiling points of the alkyloxy-ethereal salts and the acidyl derivatives, the former were eliminated in the course of fractional distillation.

With regard to the mechanism of the reaction by which the alkyloxy-acid is produced, we are unable at present to say anything definite. It is well known that alcohols and alkyl haloids interact when heated to a sufficiently high temperature, yielding halogen acid and ether (*Annalen*, 1864, 131, 55), but so far as we know the analogous formation of an alkyloxy-acid by the action of an alkyl halide on a hydroxy-acid or its ethereal salt has not been observed, and it seems unlikely that a direct action of this kind should occur at the temperature we employed. We made some experiments, the results of which tend to negative the idea that the reaction is merely of the nature referred to. Active ethylic lactate made by the sulphuric acid method was heated at 100° in a closed tube with ethylic iodide. The product distilled irregularly and was coloured with iodine, which was removed by shaking the liquid with mercury. The activity had decreased somewhat, from which we conclude that ethoxypionic acid had not been formed. Another experiment\* in which lead oxide was added with the view of removing the hydriodic acid, supposed to be formed, from the sphere of chemical action, gave also a negative result. The fact that isopropyl iodide was more active than the primary iodide in producing the alkyloxy-acids suggested the idea that these acids might possibly be

\* Ethylic malate was used in this case.



formed by the addition of the alkylene resulting from the decomposition of the iodide, according to the equation



The reaction is certainly a very improbable one, and as a matter of fact we found on trial that the activity of ethylic malate was not altered by passing ethylene through it at 100°. We are at present engaged in some experiments which we think may throw some light on the reaction and may perhaps also furnish a method of preparing the active alkyloxy-acids directly from the active hydroxy-acids.

In conclusion, we may draw attention to a fact, established by our experiments, which is of some importance on account of its stereochemical bearings. The replacement of the alcoholic hydrogen of malic and lactic acids by alkyl groups produces a very great change of activity. From considerations based on the ionic rotations of malic and ethoxysuccinic acid (Trans., 1895, 67, 982), it was concluded that a change of sign of activity accompanied the substitution in question, but this conclusion now appears to be incorrect. The rotations, of the ethereal salts of the alkyloxy-acids, produced in the reactions described, are in the same sense as those of the ethereal malates and lactates together with which they are formed.

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### XXX.—*The Optical Rotations of Methylic and Ethylic Tartrates.*

By (the late) JAMES WYLLIE RODGER and J. S. STRAFFORD BRAME.

THE intention of the authors at the commencement of this research was to prepare the ethereal tartrates in a high state of purity and investigate the influence of different alkyl radicles on the optical activity at varying temperatures. In attempting to prepare dimethyl- and diethyl-tartrates by two distinct methods, it was found that widely different rotations were exhibited by the compounds obtained by saturating an alcoholic solution of tartaric acid with hydrochloric acid, or heating the acid and alcohol in sealed tubes, and by those obtained from the action of the alkyl iodide on silver tartrate.

Similar differences have been noticed in the case of lactates by J. Wallace Walker (Trans., 1895, 67, 914), and for malates and lactates by Purdie and Williamson (Trans., 1896, 69, 818).

Owing to the lamented death of Mr. J. W. Rodger and the appointment of the other author to a different laboratory, it has been



impossible to carry out the work as intended, but there is sufficient of interest and importance to justify the publication of what has been done.

*Preparation.*

*First method.*—By saturation with gaseous hydrogen chloride. The method of Anschütz and Pictet was used. A saturated solution of tartaric acid in ethylic alcohol, kept cool by ice, was thoroughly saturated with dried hydrogen chloride; air was then rapidly drawn through it for some time, and finally the excess of hydrogen chloride, alcohol, and water quickly distilled off under reduced pressure. The residue was again dissolved in alcohol and the process repeated, allowing the saturated solution to stand five weeks; finally, the product was fractionated under diminished pressure. After the fractionation had proceeded some time, much charring took place, the pressure rose rapidly, the temperature fell, and a limpid liquid distilled. On examination, this liquid readily gave the iodoform test, and, although not completely purified owing to its small amount, the results of a combustion fully agree with those required for ethylic alcohol; moreover, its boiling point ( $78^{\circ}$ ) confirms this supposition. Ethylic tartrate No. 1 was prepared by this method.

*Second method.*—Freundler's was adopted, which differs from the preceding in evaporating the alcoholic solution of the acid until a crystalline mass (supposed to contain ethylic hydrogen tartrate) is obtained, dissolving this in alcohol and saturating as before. No. 2 specimen of ethylic tartrate was prepared in this way.

*Third method.*—By heating tartaric acid or the alkylic hydrogen tartrate in sealed tubes with alcohol; the yield, however, is exceedingly small if tartaric acid is merely heated with alcohol in a sealed tube. The method used was to heat the acid with twice its weight of the particular alcohol in a reflux apparatus for 4 hours, and then rapidly distil off the alcohol, and the water formed, under reduced pressure. The residue of mono-substituted ethereal salt was then dissolved in more alcohol, and the mixture heated in sealed tubes for 5 hours at  $150$ — $160^{\circ}$ ; the contents of tube were transferred to a flask, the excess of alcohol and the water formed quickly removed as before, and the ethereal salt fractionated under diminished pressure. By this method, methylic and ethylic tartrates are readily prepared, and the yield is good.

The ethylic tartrates Nos. 3, 4, and methylic tartrates Nos. 1, 2 were prepared in this way.

*Fourth method.*—By the action of an alkyl iodide on silver tartrate. An excess of iodide was boiled in a reflux apparatus, silver tartrate, which had been dried thoroughly in a vacuum, was added in small

quantities at a time, and the mixture boiled for 2 hours after the whole of the tartrate had been added ; the excess of iodide was then distilled off, the residue extracted several times with pure dry ether or benzene, the solvent distilled off, and in the case of ethylic tartrate the residue distilled under diminished pressure. For methylic tartrate, benzene was used as the solvent, and after partial evaporation crystals of methylic tartrate were obtained on adding some solid tartrate from another preparation. It is most difficult without a nucleus to obtain the methylic tartrate in the crystalline form, the liquid being very viscous. It was found necessary to distil the tartrate in every case, for crystallisation, even although carried out several times, did not give a sufficiently clear product for measurements of the rotation. When this method is adopted, it is essential that the materials used be as dry as possible, otherwise little or no yield is obtained.

The ethereal salts prepared by this method were always so coloured with iodine as to render accurate polarimetric measurements impossible, their solutions were therefore shaken with mercury, filtered, the solvent distilled off, and the residue fractionated under reduced pressure.

Ethylic tartrates Nos. 5, 6, 7, and methylic tartrates Nos. 3, 4, 5, 6, were prepared from silver tartrate.

#### *Observation of the Angle of Rotation.*

A half-shadow instrument by Laurent was used, the vernier giving readings to five seconds. The samples were contained in glass tubes similar to those used by Rodger and Watson (*Trans. Roy. Soc.*, 1895, 186, pt. ii, p. 626), which ensured the tubes being full at any temperature ; the tubes were enclosed in a water jacket, and the observations were always made at 20° or very close to that temperature. Every care was taken that the readings should be accurate, the tubes when filled being left for some time in the apparatus to ensure the contents having the proper temperature ; this is important, as W. H. Perkin, sen., has pointed out that the rotation of these ethereal salts is very appreciably affected by change of temperature (*Trans.*, 1887, 51, 363). The experience of the authors fully bears this out.

The final results obtained are given in the tables (p. 304). A number of observations for each sample were taken, distilling each time until a pure product was obtained.

Frankland and Wharton (*Trans.*, 1896, 69, 1310) found that methylic tartrate prepared by Freundler's method gave a rotation of 2.74° in a tube 1 dm. long.

It will be noticed at once that the salts prepared by the silver tartrate method invariably give a much higher rotation than when

*Methylic tartrate.*

Method of preparation.	Specimen. No.	$[\alpha]_D^{20}$ Tartaric acid.	Temperature of distillation.	Pressure during distillation.	Temperature of observation.	$a/l$ for 1 dm.
Sealed tube	1	13.32	169—171°	19—20 mm.	20.2°	2.785
„ „	2	13.47	168.5—170°	17—23 mm.	20.3	2.804
Silver salt	3	13.47	163.5—168°	14—17 mm.	20	3.64
„ „	4	13.32	164—166°	13.5—18 mm.	20.1	3.127
„ „	5	13.47	165—169°	15—19.5 mm.	19.8	3.30
„ „	6	13.32	159—162.5°	9—13 mm.	19.9	4.038

*Ethylic tartrate.*

Method of preparation.	Specimen. No.	$[\alpha]_D^{20}$ Tartaric acid.	Temperature of distillation.	Pressure during distillation.	Temperature of observation.	$a/l$ for 1 dm.
Anschütz	1	13.32	185—177°	31—22 mm.	20.1°	9.37
Freundler	2	13.32	185—191°	37—43 mm.	20	9.31
Sealed tube	3	13.32	169—172°	14—17 mm.	20	9.25
„ „	4	13.32	172—178°	22—21 mm.	19.9	9.22
Silver salt	5	13.32	161.5—163.5°	20 mm.	20	14.33
„ „	6	13.47	171.5—172°	18—20 mm.	20	14.91
„ „	7	13.32	174—176°	17—20 mm.	19.8	14.37

prepared by either of the other methods; the differences here are, indeed, much greater than those observed by Purdie and Williamson in the case of the methylic and ethylic malates and lactates. Further, it will be seen that the compounds produced by the sealed tube method have nearly the same rotatory power as those produced by saturating with gaseous hydrogen chloride.

Again, the rotation for the different samples of methylic and ethylic tartrates produced by the silver method is by no means constant, varying in a manner which cannot easily be accounted for, because, as far as possible, the preparations were similarly conducted. Purdie and Williamson found that the rotation of ethylic lactate prepared from the silver salt differed from that of the same compound prepared in a similar way by J. Wallace Walker, confirming the experience of the authors that the product formed is variable in composition when this method is employed.

In order to determine any difference between the ethereal salts produced by the silver method and those produced by other methods, the following experiments were carried out.

1. 4.5 grams of methylic tartrate (No. 1) and the same weight of

specimen (No. 3) were treated under exactly the same conditions with a definite volume of sodium hydroxide solution containing more than sufficient soda to decompose the tartrates. After carefully boiling for some time, the solutions were each made up to 100 c.c., and the rotations observed.

	No. 1.			No. 3.		
Length of tube, 5 dem.....	7°	16'	35"	7°	20'	15"
"    "    "    4 dem.....	5°	48'	35"	5°	49'	50"

Thus, on decomposition by an alkali, there is practically no difference in the rotations of the products.

2. The refractive indices of two samples of methylic tartrate and two of ethylic tartrate were taken; the measurements were made under comparable conditions, but the figures given must not be taken as the exact refractive index of the tartrates.

Methylic tartrate.	$\alpha/l$	$\mu$	Ethylic tartrate.	$\alpha/l$	
No. 1	2.785	1.452	No. 1	9.37	1.444
No. 5	3.30	1.452	No. 6	14.91	1.443

3. Combustions were made of two specimens of each of the compounds; the results can only be compared one with the other, since the substances are somewhat hygroscopic, and as the samples had been prepared some months previously, a small amount of water had been taken up, causing decomposition, and thus accounting for the low carbon. Before weighing for the combustion, the substance was kept in a vacuum over sulphuric acid, it being impossible to redistil.

Methylic tartrate.	Carbon.	Hydrogen.	Ethylic tartrate.	Carbon.	Hydrogen.
No. 1	40.16	5.58	No. 1	45.69	6.82
No. 3	40.01	5.55	No. 7	45.82	6.83
	40.50	5.62 (theoretical)		46.65	6.80 (theoretical)

The abnormal optical results recorded may be explained on three different hypotheses. First, the low activity of the ethereal salts prepared by the common method of etherification may be due to racemization. Second, the compounds obtained from the silver salts may be isomeric with, and more active than, those prepared by the other methods; or, third, they may be contaminated with small quantities of some more active substance.

The first explanation is precluded by the constancy of the rotations of the specimens prepared by us by three different methods, and by the fact that our measurements also agree with those of other observers. The second explanation, however improbable, is supported by the remarkable result that the two specimens of methylic tartrate of different activity, gave, on hydrolysis, products which showed

almost exactly the same rotation. With regard to the third hypothesis, Purdie and Lander, in a "Preliminary Note on the Action of Alkyl Iodides on Silver Malate" (*Proc.*, 1896, 170, 221), ascribe the higher rotation in the case of malates to the presence of "small quantities of the ethereal salts of the highly active alkyloxy-acids." The same explanation may hold in the case of the alkyl tartrates, the hydrogen of one or both of the alcoholic hydroxyl groups having been replaced by alkyl radicles during the transformation of the silver tartrate. These derivatives of active tartaric acid not yet having been prepared, their activity is unknown; they must in this case be highly active substances, otherwise their presence in such quantity as to account for the great rise in activity produced would have been detected by analysis. On this hypothesis, the identity of the rotations of the products of hydrolysis of the two methylic tartrates must be a coincidence; a great difference between them was probably not to be expected. Judging from the known optical relations of the malates and monalkyloxysuccinates, it is very likely that the sodium salts of tartaric acid and of the alkylated tartaric acids referred to would show a much smaller difference of activity than the ethereal salts of the corresponding acids. That the rotations of the products of hydrolysis of the ethereal salts prepared by the two different methods should coincide so closely is, however, very remarkable.

It has not been possible, so far, to prove the existence of these compounds in either of the ethereal salts prepared by the silver process, and the only promising method of doing so appears to be successive recrystallisation of the methylic tartrate from benzene. As the accompanying figures show, this recrystallisation lowers the rotation considerably.

Methylic tartrate. No. 6.	Temp. of observation.	$\alpha/l$
1st crystallisation	19.9°	4.038
2nd       ,,	19.7°	3.886
3rd       ,,	20.05°	3.561

It is therefore probable that the mother liquor, if examined, would be found to contain the more active constituent. Unfortunately, it has not been possible to resume the experimental work, and any further explanation or proof of the cause of difference will no doubt be supplied by Dr. Purdie and Mr. Lander, who have undertaken to investigate the question further.

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# XXXI.—Position-Isomerism and Optical Activity: the Comparative Rotatory Powers of Diethylic Monobenzoyl and Mono-toluyltartrates.

By PERCY FRANKLAND, F.R.S., and J. MCCRAE, Ph.D., late Priestley Scholar in Mason University College, Birmingham.

THE object of this investigation was twofold; firstly, to pursue the inquiry already commenced by one of us as to the relationship between optical activity and position-isomerism (Trans., 1896, 69, 1309 and 1583); and, secondly, to obtain information as to the rotatory power of the monacidyl substitution products of the ethereal tartrates, which have hitherto received comparatively little attention.

In the papers cited above, it was shown that, both in the case of methylic and of ethylic tartrate, the greatest influence is exerted on the rotation by the introduction of two para-toluyyl groups and the least by two ortho-toluyyl groups, whilst the influence of two meta-toluyyl groups is intermediate between that exerted by the two para- and the two ortho-groups respectively; again, the influence of two benzoyl groups was found to be greater than that of the ortho- and less than that of the meta-toluyyl groups.

This relationship does not appear, however, to be a perfectly general one, as is shown by the following results, which have been obtained by other observers in the case of similar series, thus

Walden (*Zeit. physikal. Chem.*, 1895, 17, 265).

(In glacial acetic solution).

Maldianilide .....	$[\alpha]_D =$	$-60.66^\circ$	concentration = 1.5
		$-58.66$	" = 0.75
Maldiorthotoluide .....	,, =	$-66.5$	" = 1.00
		$-65.0$	" = 2.00
Maldiparatoluide .....	,, =	$-70.0$	" = 1.00

Welt (*Ann. Chim. Phys.* [vii], 1895, 6, 142).

Phenyl amyl oxide.....	$[\alpha]_D =$	$+4.01^\circ$	(in liquid state).
Ortho-cresyl amyl oxide .....	,, =	$+3.86$	,,
Meta- ,, .....	,, =	$+3.93$	,,
Para- ,, .....	,, =	$+4.26$	,,

Guye and Chavanne (Guye, *Bull. soc. chim.*, [iii], 15, 298).

Amylic benzoate.....	$[\alpha]_D =$	$+4.96^\circ$	(in liquid state).
,, ortho-toluate.....	,, =	$+4.55$	,,
,, para- ,, .....	,, =	$+5.20$	,,
,, phenacetate .....	,, =	$+3.84$	,,
,, phenylpropionate.....	,, =	$+2.15$	,,

Goldschmidt and Freund (*Zeit. physikal. Chem.*, 1894, **14**, 394).

(In chloroform solution.)

Amylic phenylcarbamate .....	$[\alpha]_D = +4.19^\circ$	concentration = 5.2478
„ ortho-tolylcarbamate .....	„ = +2.66	„ = 5.3277
„ meta- „ .....	„ = +3.85	„ = 5.3058
„ para- „ .....	„ = +4.47	„ = 5.2765

N.B.—The above compounds were prepared from an amylic alcohol  $[\alpha]_D = -4.29^\circ$  ( $t = 21^\circ$ ,  $d = 0.8153$ ).

(Chloroform solution.)

Menthyl phenylcarbamate.....	$[\alpha]_D = -77.21^\circ$	concentration = 5.6085
„ ortho-tolylcarbamate.....	„ = -65.88	„ = 5.6157
„ meta- „ .....	„ = -71.43	„ = 5.5791
„ para- „ .....	„ = -72.30	„ = 5.6177

Menthol in alcoholic solution (concentration = 5)  $[\alpha]_D^{25} = -49.4^\circ$ .

Carbanilido- <i>r</i> -carboxime .....	$[\alpha]_D = +33.34^\circ$	concentration = 7.7614
„ „ .....	„ = +31.67	„ = 2.7205
Carbortho-toluido- „ .....	„ = +28.19	„ = 7.8088
„ „ .....	„ = +27.40	„ = 2.7547
Carbometa-toluido- „ .....	„ = +29.94	„ = 7.7146
„ „ .....	„ = +29.79	„ = 2.7402
Carbopara-toluido „ .....	„ = +32.52	„ = 9.4485
„ „ .....	„ = +30.75	„ = 2.7106

Benzoyl- <i>r</i> -carboxime .....	$[\alpha]_D = +26.64^\circ$	concentration = 9.1058
Ortho-toluyyl- „ .....	„ = +27.08	„ = 9.1942
Meta-toluyyl- „ .....	„ = +26.86	„ = 10.0169
Para-toluyyl- „ .....	„ = +23.44	„ = 9.2950
Phenacetyl- „ .....	„ = +40.63	„ = 7.7806

N.B.—The last product was not obtained in a state of purity, the real rotation would be somewhat higher. The above figure, however, shows how entirely different is the rotatory effect of the phenacetyl group from that of the metameric toluyyl-groups; in fact, in the case of the tartrates and glycerates, the phenacetyl group much resembles the acetyl group itself in its rotatory effect.

(Chloroform solution.)

Ortho-bromobenzoyl- <i>r</i> -carboxime...	$[\alpha]_D = +25.96^\circ$	concentration = 5.4687
Meta- „ „ .....	„ = +18.24	„ = 5.5132
Para- „ „ .....	„ = +14.90	„ = 5.4965

Ortho-nitrobenzoyl- <i>r</i> -carboxime ...	$[\alpha]_D = 0^\circ$	concentration $\begin{cases} = 4.7044 \\ = 4.5575 \end{cases}$
Meta- „ „ .....	„ = +20.68	„ = 4.5845
Para- „ „ .....	„ = +17.33	„ = 4.5648

N.B.—The inactivity of the ortho-compound is very remarkable, as, on hydrolysis with sodium hydroxide, a dextrorotatory, and not an inactive, carboxime was obtained. From analogy, the ortho-compound should in this case have the highest rotation of the three.

All the above carboxime derivatives were prepared from a carboxime of rotation  $[\alpha]_D = +39.62^\circ$  (in absolute alcoholic solution of concentration = 9.8398).

Rawitzer (*Thesis Zurich*, 1896, 25 ; Guye, *Bull. soc. chim.*, [iii], 15, 1158).

	Concentration of acetic acid solution.	$[\alpha]_D$ .
$\beta$ -Methyladip-anilide .....	1.76	+25.9°
„ ortho-toluide .....	0.35	+58.2
„ meta- „ .....	1.52	+11.0
„ para- „ .....	1.57	+35.9

Excepting in the last two series mentioned, the rotatory relationship between the ortho-, meta-, and para-compounds is the same throughout, whilst the relationship between the phenyl and the three tolyl compounds is subject to variation in the several series. It should be observed that only in two out of the above ten series were the polarimetric determinations made on the liquid substances themselves, solutions having been employed in the other cases.

In the series which forms the subject of the present communication, the rotations have throughout been determined both in solution and on the substances in a fused state, as well as over a wide range of temperature.

The monacidyl ethereal tartrates have formed the subject of investigations by Perkin (*Trans.*, 20, 138), who prepared ethylic monobenzoyltartrate and ethylic monacetyltartrate, without, however, determining their rotatory power, and more recently by Guye and Fayollat (*Bull. soc. chim.*, 1895, [iii], 13, 190), who give rotations in ether solution for the following compounds.

	$[\alpha]_D$ .
Ethylic tartrate.....	+5.25° (in ether solution).
„ monacetyltartrate .....	+2.4 „
„ monopropionyltartrate .....	+2.3 „
„ monobutyryltartrate .....	+1.8 „
„ monobenzoyltartrate .....	+1.5 „

And in alcoholic solution for the following.

	$[\alpha]_D$ .
Isobutylic tartrate .....	+11.8° (in alcoholic solution).
„ monacetyltartrate .....	+7.8 „
„ monobutyryltartrate .....	+9.7 „
„ monobenzoyltartrate .....	+11.5 „

Only one of the above compounds, namely, ethylic monobenzoyltartrate, has been prepared by us also and a comparison of our results with those of Guye and Fayollat will be found on p. 312.

The preparation of the monacidyl substituted tartrates is attended with peculiar difficulty owing to the tendency for diacidyl products to be simultaneously formed, even when only a small proportion of acid chloride is made to act on a very large excess of tartrate. The subsequent separation of the monacidyl from the diacidyl tartrate can only be secured by a long series of crystallisations.

We had hoped to have been able to prepare a complete series of monacidyl derivatives from both ethylic and methylic tartrates, but we found that, in the case of the methylic tartrate, the tendency to form the diacidyl compound was so predominant that we have had to abandon for the present the preparation of the monacidyl methylic tartrates.

*Preparation of Ethylic Tartrate.*

Large quantities of this substance had to be prepared for the purposes of this investigation. In the first instance, we adopted the hydrochloric acid method, as described by one of us (*Trans.*, 1896, **69**, 1310), but latterly we replaced this by the sealed tube method as more expeditious, and which, as far as we are aware, has not hitherto been employed for the preparation of the ethereal salts of tartaric acid.

Ethyltartaric acid is first prepared by dissolving 50 grams of tartaric acid, which has been dried in the steam oven, in 150 grams of absolute alcohol; the solution is allowed to remain overnight, the excess of alcohol being then distilled off on a water bath, and the residue dried in an open dish in the steam oven for 3 hours. About 20—25 grams of the syrup thus obtained are placed in a tube with 40 c.c. of absolute alcohol, and after sealing the tube it is heated at  $160^{\circ}$  for 4—5 hours. The alcohol is then distilled off, and the ethereal salt rectified under reduced pressure. The rotation of the preparation was  $\alpha_D = +9.323^{\circ}$ ,  $t = 20^{\circ}$ ,  $l = 1$ , almost exactly the same, but, if anything, slightly higher than that which we have generally obtained with the salt prepared by the hydrochloric acid method.

*Diethylic monobenzoyltartrate.*

In the first instance, we endeavoured to prepare this according to the instructions given by Perkin (*Trans.*, 1867, **20**, 138), but the product obtained had a melting point lower by  $0.5^{\circ}$  than his, and this was the case even after it had been recrystallised from light petroleum, a process of purification to which Perkin's substance had not been submitted. Our substance, moreover, solidified under water in about 6 days, whilst Perkin found that 3 weeks were necessary.

On analysis, our substance proved to be too rich in carbon for the monobenzoyl compound, thus

I.	H = 5.79 per cent.	; C = 58.96 per cent.
II.	H = 5.77    „    „	C = 58.82    „    „

were found, whilst diethylic monobenzoyltartrate requires

$$H = 5.81 \text{ per cent.}, \text{ and } C = 58.06 \text{ per cent.}$$

As the excess of carbon was doubtless due to the presence of diethylic dibenzoyltartrate, we modified the method of preparation in

the following manner, so as to reduce to a minimum the chances of this latter compound being formed.

Thirty grms of diethylic tartrate ( $[\alpha]_D^{20} = +7.643$ ) were heated on the water bath, and to it were added drop by drop 14 grams of benzoyl chloride, the whole being agitated while the acid chloride was being added; thus at no time was the latter even locally in excess. The mixture was then heated on the water bath for 3 hours until the evolution of hydrochloric acid fumes had ceased; when cold, it was vigorously agitated with a solution of sodium carbonate, and, after washing with water, it was dissolved in ether and the ethereal solution shaken for 2 hours with a solution of sodium carbonate. The ethereal solution, after separation, was well washed with water and then dried over potassium carbonate; on evaporating the ether, a yellowish oil having a greenish fluorescence was left. This was then covered with a layer of water, and in the course of an hour or two almost colourless crystals began to separate. The water, which was very yellow, was changed several times until the mass had become solid and colouring matter was no longer extracted, the mass being always well pressed under the water before the latter was changed. The solid, which melted at  $59^\circ$  when dried, was fractionally extracted with, and crystallised from, light petroleum. Six crops of crystals were thus obtained, one and all of which had a melting point of  $64.5$ — $65^\circ$ , (Perkin gives  $64^\circ$ ). The yield was 12 grams. Further recrystallisation from light petroleum did not alter the melting point.

On combustion, the following results were obtained.

0.1665 gave 0.3545  $\text{CO}_2$  and 0.0880  $\text{H}_2\text{O}$ .  $\text{C} = 58.07$ ;  $\text{H} = 5.87$ .

Diethylic monobenzoyltartrate,  $\text{C}_{15}\text{H}_{18}\text{O}_7$ , requires  $\text{H} = 5.81$ ;  
 $\text{C} = 58.06$  per cent.

Diethylic dibenzoyltartrate,  $\text{C}_{22}\text{H}_{22}\text{O}_8$ , requires  $\text{H} = 5.31$ ;  
 $\text{C} = 63.77$  per cent.

With this first preparation melting at  $64.5$ — $65^\circ$ , the following polarimetric observations were made.

*Rotation of Diethylic Monobenzoyltartrate (First Preparation).*

Temp.

99°	$[\alpha]_D = \frac{+7.585}{0.4243 \times 1.1297} = +15.82^\circ$
67	$'' = \frac{+8.29}{0.4243 \times 1.1630} = +16.79$
42	$'' = \frac{+8.715}{0.4243 \times 1.191} = +17.27$
109	$'' = \frac{+7.36}{0.4243 \times 1.1195} = +15.49$





Temp.		$[\delta]_D$
38°	$[\alpha]_D = \frac{+12.00}{0.4985 \times 1.1930} = +20.18^\circ$	+154°
24	$[\alpha]_D = \frac{+12.47}{0.4985 \times 1.2075} = +20.71$	+159
135	$[\alpha]_D = \frac{+8.91}{0.4985 \times 1.0920} = +16.36$	+117
[180	$[\alpha]_D = \frac{+8.53}{0.4985 \times 1.0465} = +16.35$	+114]*

The following density determinations were actually made.

$$d_{56^\circ/4^\circ} = 1.1701. \quad d_{72^\circ/4^\circ} = 1.1535. \quad d_{99^\circ/4^\circ} = 1.1297. \\ d_{141^\circ/4^\circ} = 1.0878.$$

At the last high temperature, the substance had suffered slight decomposition, indicated by its becoming somewhat brown. The rotation was, therefore, again determined at 100°, but it had not appreciably altered.

In the preparation and recrystallisation of diethylic monobenzoyltartrate, an oil which would not solidify was obtained; this gave a rotation

$$\alpha_D = -37.97^\circ (t = 100^\circ, l = 1).$$

0.1795 gave 0.4000 CO<sub>2</sub> [H<sub>2</sub>O lost]. C = 60.78.

Theory for diethylic monobenzoyltartrate, C = 58.06 per cent.

“ “ “ dibenzoyltartrate, C = 63.77 per cent.

It would thus appear that this oil was a mixture of the mono- and the di-benzoyltartrate, a conclusion which is in harmony with the fact that the rotation for diethylic dibenzoyltartrate is given by P. Frankland and Wharton (Trans., 1896, 69, 1586) as

$$[\alpha]_D^{100^\circ} = \frac{-30.16}{0.44 \times 1.1280} = -60.77^\circ$$

As Guye and Fayollat did not remove this oil, it affords strong presumptive evidence that the very low positive rotation ( $[\alpha]_D = +2.90^\circ$ ), which they found for diethylic monobenzoyltartrate was due to its presence.

In the case of the diethylic monotoluyltartrates (ortho- and meta-) we have similarly obtained uncrystallisable oils in addition to the solid ethereal salts themselves, whilst in the case of the para-compound a solid impurity was present (see p. 314).

#### *Diethylic Mono-paratoluyltartrate.*

Forty grams of ethylic tartrate ( $[\alpha]_D^{20} = +7.643^\circ$ ) were heated on a water bath and 15 grams of paratoluyyl chloride were added drop by

\* Owing to the liquid having become coloured at this temperature, the accuracy of this polarimetric result is somewhat doubtful.

drop, the liquid being well shaken the whole time; after the addition of the acid chloride, the mixture was heated on the water bath for 3 hours longer. When cool, it was shaken with a solution of sodium carbonate, but the whole immediately solidified; the solid mass was broken up and again agitated for some time with the solution of sodium carbonate. The aqueous part was then poured off, the solid dissolved in ether, and the ethereal solution shaken for 5 hours with a solution of sodium carbonate. After separating, the ethereal liquid was thoroughly washed with water and dried over potassium carbonate. On evaporating the ether, the residue was left in the form of prismatic crystals melting at  $89.5^{\circ}$ .

0.1905 gave 0.4170  $\text{CO}_2$  and 0.1050  $\text{H}_2\text{O}$ .  $\text{C} = 59.70$ ;  $\text{H} = 6.12$ .

Diethylic monoparatoluyltartrate,  $\text{C}_{16}\text{H}_{20}\text{O}_7$ , requires  $\text{C} = 59.26$ ;  
 $\text{H} = 6.17$  per cent.

Diethylic diparatoluyltartrate,  $\text{C}_{24}\text{H}_{26}\text{O}_8$ , requires  $\text{C} = 65.16$ ;  
 $\text{H} = 5.88$  per cent.

The above analysis shows that doubtless some diparatoluyltartrate was present. The crystals were powdered and heated with a quantity of light petroleum insufficient to dissolve the whole; the solution on being poured off deposited crystals melting at  $87^{\circ}$ . This treatment was repeated in all five times, and the fifth time the whole was dissolved. The melting points of the several crops of crystals thus obtained were II.  $93.5^{\circ}$ , III.  $94^{\circ}$ , IV.  $94^{\circ}$ , and V.  $94^{\circ}$ . After further repeated fractional crystallisation (in all 17 fractions were obtained), there was a yield of 14 grams of substance having a melting point of  $94^{\circ}$ , and a small quantity melting at  $85-87^{\circ}$ . The prismatic crystals melting at  $94^{\circ}$ \* were submitted to combustion with the following result.

0.1680 gave 0.3650  $\text{CO}_2$  and 0.0970  $\text{H}_2\text{O}$ .  $\text{C} = 59.25$ ;  $\text{H} = 6.41$ .

Diethylic monoparatoluyltartrate,  $\text{C}_{16}\text{H}_{20}\text{O}_7$ , requires  $\text{C} = 59.26$ ;  
 $\text{H} = 6.17$  per cent.

With this substance, the following polarimetric observations were made.

*Rotation of Diethylic Monoparatoluyltartrate.*

[(Length of polarimeter tube in each case was 49.85 mm.)]

At $100^{\circ}$	$[\alpha]_D = \frac{+8.79}{0.4985 \times 1.1122}$	$= +15.85^{\circ}$	$\left. \begin{array}{l} [\delta]_D \\ +117^{\circ} \end{array} \right\}$
,, 109	,, $= \frac{+8.51}{0.4985 \times 1.1053}$	$= +15.44$	$\left. \begin{array}{l} \\ +113 \end{array} \right\}$

\* The melting point of diethylic di-paratoluyltartrate was found to be  $92-93^{\circ}$  (P. Frankland and Wharton, 1896, 69, 1314).

At 138°	$\frac{+7.88}{0.4985 \times 1.0835}$	= +14.59°	$\frac{+7.88}{0.4985 \times 1.0835}$	[δ] <sub>b</sub> +106°
,, 180    ,,	$\frac{+7.015}{0.4985 \times 1.052}$	= +13.38	$\frac{+7.015}{0.4985 \times 1.052}$	+95

After this series of determinations had been made, the rotation was again taken at 100° with substantially the same result as above. The substance was also again twice recrystallised from light petroleum, and the rotation taken at 100° with almost exactly the same result,

$$[\alpha]_D^{100} = \frac{+8.775}{0.4985 \times 1.1122} = +15.83^\circ.$$

The density determinations actually made were  $d_{100^\circ/4^\circ} = 1.1122$ , and  $d_{137.5^\circ/4^\circ} = 1.0839$ .

In order to further confirm the above results, another preparation was made, using in this case as much as 102 grams of diethylic tartrate to 15.5 grams of paratoluyyl chloride. After six recrystallisations from light petroleum, the melting point was constant at 93.5—94°, and the rotation at 100° was  $[\alpha]_D^{100} = \frac{+8.74}{0.4985 \times 1.1122} = +15.77^\circ$ , a result, therefore, practically identical with the above.

#### *Diethylic Monorthotoluyyltartrate.*

This was prepared in the same manner as described above for the para-compound, but, on evaporating the ether, the ethereal salt was left as an oil with a slightly yellow tinge, the further purification of which was attended with much difficulty. Thus

*First Preparation.*—In this, 20 grams of ethylic tartrate to 15 grams of orthotoluyyl chloride were employed. An attempt was made to distil the oily product under reduced pressure, but this resulted in its apparent total decomposition.

*Second Preparation.*—In this, 40 grams of ethylic tartrate and 15 grams of orthotoluyyl chloride were employed; the oil was dissolved in methylated spirit and precipitated again by water, extracted with chloroform, the chloroform solution dried, and the chloroform evaporated. After drying the oil in a vacuum, its rotation was found to be

$$\alpha_D = +1.064^\circ, t = 20^\circ, l = 49.92 \text{ mm.}$$

It was then treated with methylated spirit, water, and chloroform, as before, after which the rotation was

$$\alpha_D = +0.106^\circ, t = 20^\circ, l = 49.92 \text{ mm.}$$

After being again submitted to the same treatment, the rotation was

$$\alpha_D = -0.562^\circ, t = 20^\circ, l = 49.92 \text{ mm.}$$

On again being submitted to this treatment, the rotation was

$$\alpha_D = -0.556^\circ, t = 20^\circ, l = 49.92 \text{ mm.}$$

It was now submitted to a similar treatment in which acetone was substituted for alcohol and ether for chloroform, the rotation now becoming

$$\alpha_D = -1.260^\circ, t = 20^\circ, l = 49.92 \text{ mm.}$$

and on repeating this treatment with acetone and ether,

$$\alpha_D = -2.581^\circ, t = 20^\circ, l = 49.92 \text{ mm.}$$

On combustion.

0.1855 gave 0.4110  $\text{CO}_2$  and 0.1065  $\text{H}_2\text{O}$ .  $\text{C} = 60.43$ ;  $\text{H} = 6.37$ .

Theory for diethylic monotoluyltartrate,  $\text{C} = 59.26$ ;  $\text{H} = 6.17$  per cent.

„ „ „ ditoluyltartrate,  $\text{C} = 65.16$ ;  $\text{H} = 5.88$  „

„ „ 80 per cent. mono- and 20 per cent. di-toluyltartrate,  
 $\text{C} = 60.42$ ;  $\text{H} = 6.12$  per cent.

It thus appeared that the methods of treatment with alcohol and with acetone respectively, instead of purifying the monotoluyyl compound, were actually leading to a concentration of the ditoluyyl compound, for the progressive rise of the rotation in the negative direction was obviously to be interpreted in this manner, since it has been shown by one of us (*loc. cit.*) that ethylic di-orthotoluyltartrate has a very high negative rotation.

*Third Preparation.*—In this, 35 grams of ethylic tartrate and 14 grams of orthotoluyyl chloride were used. The treatment of the product was the same as that described in detail under “*Second preparation*” (see pp. 315 *et seq.*), but the rotation was taken of the oil left on evaporating the ether, and without the further operations described under “*Second preparation.*” The rotation was

$$\alpha_D = +0.739^\circ, t = 20^\circ, l = 49.92 \text{ mm.}$$

0.1865 gave 0.4065  $\text{CO}_2$  and 0.1060  $\text{H}_2\text{O}$ .  $\text{C} = 59.46$ ;  $\text{H} = 6.31$ .

Theory for 96.5 per cent. mono- and 3.5 per cent. di-toluyltartrate,  
 $\text{C} = 59.46$ ;  $\text{H} = 6.15$  per cent.

*Fourth Preparation.*—In this, we further increased the excess of ethylic tartrate, of which 71 grams were used to 15 grams of orthotoluyyl chloride. The oil obtained in the same way as in the third preparation exhibited the rotation

$$\alpha_D = +4.59^\circ, t = 20^\circ, l = 49.92 \text{ mm.}$$

*Fifth Preparation.*—In this, the proportion of ethylic tartrate was still further exaggerated, 95 grams to 15 grams of orthotoluyyl chloride being employed. The oil obtained as in the third and fourth prepara-



tions gave a slightly greater positive rotation than in the fourth preparation, thus

$$\alpha_D = +4.83^\circ, \quad t = 20^\circ, \quad l = 49.92 \text{ mm.},$$

showing that, in all probability, it was richer in the monotoluy compound than any of the previous ones.

After about seven weeks, this fifth preparation solidified, whilst no crystals had appeared in the others, although they were considerably older. The previous preparations were now sown with crystals, and after about three days the fourth solidified, whilst after thirty days the third had only partially done so, and in the second only a very slight propagation of the crystallisation was observable.

The fifth preparation was further treated as follows. After being spread for three days on biscuit porcelain, it had assumed a beautifully white appearance, and now exhibited the rotation

$$\alpha_D = +6.02^\circ, \quad t = 100^\circ, \quad l = 49.85 \text{ mm.}$$

The solid was then boiled with light petroleum (boiling up to  $70^\circ$ ) sufficient to dissolve only about one-half of it. The filtered solution, on cooling, deposited an oil; the petroleum was then evaporated, the last traces being removed from the residual oil in the vacuum desiccator. Its rotation was found to be

$$\alpha_D = +6.03^\circ, \quad t = 100^\circ, \quad l = 49.85 \text{ mm.}$$

The part which had not dissolved in the light petroleum had a rotation

$$\alpha_D = +6.04^\circ, \quad t = 100^\circ, \quad l = 49.85 \text{ mm.},$$

showing that no further purification had been effected by the treatment with petroleum.

The crystals obtained from the part which had been dissolved in light petroleum melted at  $32.5^\circ$ , and on combustion the following results were obtained.

0.3095 gave 0.6705  $\text{CO}_2$  and 0.1735  $\text{H}_2\text{O}$ .  $\text{C} = 59.10$ ;  $\text{H} = 6.23$ .

Diethylic mono-orthotoluytartrate,  $\text{C}_{16}\text{H}_{20}\text{O}_7$  requires  $\text{C} = 59.26$ ;  $\text{H} = 6.17$  per cent.

The fourth preparation, which, as stated above, had also solidified, was very green, but after being spread on biscuit porcelain for about ten days the colour had entirely disappeared. It was now dissolved in ether, the solution dried with potassium carbonate, and after removing the ether by evaporation, the rotation was found to be

$$\alpha_D = +6.01^\circ, \quad t = 100^\circ, \quad l = 49.85 \text{ mm.}$$

The substance was then treated with an insufficient quantity of low

boiling light petroleum, as in the case of the fifth preparation, and the rotation of the part which had been dissolved in the petroleum was found to be

$$\alpha_D = +6.03^\circ, \quad t = 100^\circ, \quad l = 49.85 \text{ mm.}$$

As the rotation of these two different preparations (four and five) was thus practically identical and constant, the more detailed investigation of the rotation was proceeded with, for which purpose that portion of the fifth preparation which had been submitted to analysis as above was employed.

*Rotation of Diethylic Mono-orthotoluylltartrate.*

Temp.			$[\delta]_D$
14°	$[\alpha]_D = \frac{+7.19}{0.4985 \times 1.1935} = +12.08^\circ$		+93°
20	$[\alpha]_D = \frac{+7.00}{0.4985 \times 1.1880} = +11.82^*$		+91
21.5	$[\alpha]_D = \frac{+6.99}{0.4985 \times 1.1872} = +11.81$		+91
32.5	$[\alpha]_D = \frac{+6.89}{0.4985 \times 1.1775} = +11.74$		+90
65	$[\alpha]_D = \frac{+6.40}{0.4985 \times 1.1462} = +11.20$		+84
100	$[\alpha]_D = \frac{+6.03}{0.4985 \times 1.1115} = +10.88$		+80
136.5	$[\alpha]_D = \frac{+5.69}{0.4985 \times 1.0749} = +10.62$		+76

The density determinations actually made were

$$d_{15^\circ/4^\circ} = 1.1933.$$

$$d_{53^\circ/4^\circ} = 1.15737.$$

$$d_{84^\circ/4^\circ} = 1.1270.$$

$$d_{110.5^\circ/4^\circ} = 1.09965.$$

*Diethylic Mono-metatoluylltartrate.*

*First Preparation.*—Guided by the experience gained in the case of the mono-orthotoluylltartrate, we employed at once a very large excess of ethylic tartrate, of which 70 grams were used to 13.5 grams of metatoluyll chloride. The method adopted was exactly similar to that described on pp. 315 *et seq.*, and on evaporating the ether a solid was in this case also obtained; this was recrystallised from light petroleum (b. p. 70°) and then fractionally dissolved from the same solvent. The

\* It is worthy of note that ethylic mono-monochloroacetyl tartrate, which has recently been obtained in a state approaching purity (Percy Frankland and Turnbull, *Trans.*, 1898, **73**, 204), possesses almost exactly the same rotation,  $[\alpha]_D^{20} = +11.44^\circ$ .

first two fractions had a melting point of  $56^\circ$ , that of the third was somewhat lower. The crystals melted to a yellowish liquid, which, on heating to  $100^\circ$  in the polarimeter tube, became so blue that no readings could be obtained. The substance was, therefore, boiled in alcoholic solution with animal charcoal, after which it was recrystallised from light petroleum. On heating to  $100^\circ$ , the blue colour did not appear, but the liquid was deep brown instead. It was again treated with animal charcoal as before, and recrystallised from light petroleum, the melting point being still  $56^\circ$ . The rotation was

$$\alpha_D = +6.91^\circ, \quad t = 100, \quad l = 49.85 \text{ mm.}$$

On recrystallisation from light petroleum in two fractions, both fractions were again found to have the same rotation as above, and on combustion the following results were obtained.

0.3215 gave 0.6982  $\text{CO}_2$  and 0.1784  $\text{H}_2\text{O}$ .  $\text{C} = 59.23$ ;  $\text{H} = 6.16$ .

Diethylic monometatoluyltartrate,  $\text{C}_{16}\text{H}_{20}\text{O}_7$ , requires  $\text{C} = 59.26$ ;  $\text{H} = 6.17$  per cent.

With this product, then, the detailed examination of the rotatory power was proceeded with.

*Rotation of Diethylic Mono-metatoluyltartrate.*

Temp.			$[\delta]_D$
100°	$[\alpha]_D = \frac{+6.91}{0.4985 \times 1.10295} = +12.57^\circ$		$+92^\circ$
14.5	$'' = \frac{+8.03}{0.4985 \times 1.1820} = +13.63$		$+105$
20	$'' = \frac{+7.96}{0.4985 \times 1.1760} = +13.59$		$+104$
54	$'' = \frac{+7.58}{0.4985 \times 1.1450} = +13.28$		$+100$
136	$'' = \frac{+6.35}{0.4985 \times 1.0690} = +11.92$		$+85$

The density determinations actually made were

$$d_{53^\circ/4^\circ} = 1.1452. \quad d_{100^\circ/4^\circ} = 1.10295. \quad d_{119^\circ/4^\circ} = 1.0846.$$

In order to make sure that no alteration in the substance had taken place by raising it to the above high temperature, the rotation was again determined at  $100^\circ$ , and found to be quite unchanged.

*Second Preparation.*—In this, 62 grams of ethylic tartrate and 12 grams of metatoluy chloride were employed. The product was purified in the same way as before, being finally recrystallised from

light petroleum until of constant rotation, which proved to be practically identical with that obtained above, namely

$$[\alpha]_D^{100} = \frac{+6.92}{0.4985 \times 1.10295} = +12.60^\circ.$$

Thus in the above series of four mono-substituted ethylic tartrates of the three isomeric toluyl compounds, the ortho- has the lowest and the para- the highest dextrorotation. This relationship between the isomeric toluyl groups and rotatory power is similar to that which has already been found by one of us (P. Frankland and Wharton, Trans., 1896, 69, 1309 and 1583) to hold good in the case of the ethylic and methylic ditoluyltartrates, but whilst in the case of the disubstituted tartrates it was found that the rotatory effect of the benzoyl group was intermediate between that of the ortho- and meta-toluy groups respectively, in the present case the rotatory effect of the single benzoyl group is greater even than that of the para-toluy group itself.

This position of the benzoyl-compound is, therefore, similar to that found in the case of the series menthyl phenylcarbamate, and of the series carbanilido-carvoxime, the rotations of which in chloroform solution are given on p. 308.

It was thought that possibly this anomalous position of the mono-benzoyl tartrate might be due to its having either a greater or less association factor than the three mono-toluy compounds, and with a view to throwing light on this point, the four substances in question were submitted to molecular weight determination by the cryoscopic method.

*Cryoscopic Determinations of Molecular Weight of Diethylic Mono-benzoyl, Monortho-toluy, Monometa-toluy, and Monopara-toluy Tartrates.*

Inasmuch as these are all hydroxy-compounds, the solvent naturally employed was glacial acetic acid.

The acetic acid used had a melting point of  $15.5^\circ$ . The usual Beckmann apparatus was used, and the bath was kept constant at  $12^\circ$  by means of water which was made to run through a metal coil surrounded with iced water. Every care was taken to prevent access of moisture to the solvent in the apparatus; the cork was coated with paraffin and the stirrer was provided with a drying apparatus.

The following results were obtained.

*Diethylic Mono-benzoyltartrate.*

Molecular weight = 310.

	Grams of solvent.	Grams of substance.	Observed depression $\Delta$ .	Grams of substance to 100 grams solvent.	Mol. weight. $\left( \frac{100 \times \text{grams subst.} \times 39}{\text{grams solvent} \times \Delta} \right)$
I.	11.949	0.5120	0.520°	4.285	321.4
II.	11.949	0.7215	0.738	6.038	319.1
III.	11.949	0.8370	0.881	7.005	310.0

*Diethylic Mono-paratoluyltartrate.*

Molecular weight = 324.

	Grams of solvent.	Grams of substance.	Observed depression $\Delta$ .	Grams of substance to 100 grams solvent.	Mol. weight.
I.	11.8185	0.4353	0.441°	3.683	326
II.	11.8185	0.6503	0.675	5.502	318
III.	11.8185	0.6978	0.748	5.904	308

*Diethylic Mono-metatoluyltartrate.*

Molecular weight = 324.

	Grams of solvent.	Grams of substance.	Observed depression $\Delta$ .	Grams of substance to 100 grams solvent.	Mol. weight.
I.	11.2642	0.4757	0.518°	4.223	318.1
II.	11.2642	0.9805	1.063	8.705	319.4
III.	11.2642	1.1202	1.283	9.945	302.3

*Diethylic Mono-orthotoluyltartrate.*

Molecular weight = 324.

	Grams of solvent.	Grams of substance.	Observed depression $\Delta$ .	Grams of substance to 100 grams solvent.	Mol. weight.
I.	9.9767	0.3737	0.460°	3.746	317.6
II.	9.9767	0.7289	0.892	7.306	319.4
III.	9.9767	0.9092	1.100	9.113	323



The above cryoscopic determinations afford little or no evidence of the existence of associated molecules in the acetic acid solution, or at most they point to a little association in the case of the benzoyl compound.

*Rotation of Diethylic Mono-benzoyl, Mono-orthotoluyll, Mono-metatoluyll, and Mono-paratoluylltartrates in Glacial Acetic Acid Solution.*

The rotation of the four substances in question was also determined in glacial acetic acid solution, two different concentrations being used in each case. The following results were obtained.

*Rotation of Substances in Glacial Acetic Acid Solution.*

Weight of solution. Grams.	Weight of substance. Grams.	Grams substance in 100 grams solution.	Density of solution at temp. of observa- tion of rotation.	Temp. of observa- tion of rotation.	Length of polari- meter tube.	$\alpha_D$ .	$[\alpha]_D$ .
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*Diethylic Monobenzoyltartrate.*

12.786	0.837	6.546	1.058	20°	1.984 dm.	+1.833°	+13.34° *
15.7728	0.7644	4.846	1.0576	19.5	1.984 ,,	+1.317	+12.95

$$[\alpha]_D^{20^\circ} = +20.86^\circ \text{ (on fused substance, calculated).}$$

*Diethylic Mono-paratoluylltartrate.*

12.7920	1.2804	10.01	1.0593	22.5°	1.0045 dm.	+1.69°	+15.87°
10.4688	0.6656	6.36	1.057	21.25	1.0045 ,,	+1.02	+15.11

$$[\alpha]_D^{20^\circ} = +19.58^\circ \text{ (on fused substance, calculated).}$$

*Diethylic Mono-metatoluylltartrate.*

8.4723	0.7176	8.47	1.056	19°	1.0045 dm.	+0.74°	+8.26°
7.9572	0.4031	5.07	1.0554	20	1.0045 ,,	+0.40	+7.45

$$[\alpha]_D^{20^\circ} = +13.59^\circ \text{ (on fused substance, experimental).}$$

*Diethylic Mono-orthotoluylltartrate.*

9.0068	1.2316	13.67	1.066	21°	1.0045 dm.	+0.72°	+4.92°
7.6393	0.6845	8.96	1.0603	21	1.0045 ,,	+0.43	+4.51

$$[\alpha]_D^{20^\circ} = +11.82^\circ \text{ (on fused substance, experimental).}$$

$$* [\alpha]_D^{20^\circ} = \frac{1.833 \times 12.786}{1.984 \times 0.837 \times 1.058} = +13.34^\circ.$$

The above table shows that all four substances exhibit very considerably lower specific rotations in glacial acetic acid solution than in the fused state, and in all cases the specific rotation increases with the concentration. Inasmuch as all four substances yielded approximately normal molecular weights by the cryoscopic method, it may reasonably be concluded that they are all approximately monomolecular in glacial acetic acid solution for the concentrations employed. But under these conditions the specific rotation of the paratoluyll was found to be greater than that of the monobenzoyl compound, so that the order of the rotations in solution approximates more to that already found by one of us for the corresponding di-substituted tartrates; but even in solution, the monobenzoyl compound has a higher rotation than the monometatoluyll compound, whilst in the case of the di-substituted tartrates the rotation of the metatoluyll is also greater than that of the benzoyl compound.

Assuming the change in specific rotation to be uniform with increasing concentration, the rotation for a concentration of 100 per cent. would be

	$[\alpha]_D^{20^\circ}$ (calculated).	$[\alpha]_D^{20^\circ}$ (fused substance).
Diethylic mono-benzoyltartrate.....	+34.78°	+20.86°
„ mono-paratoluylltartrate .....	+34.60	+19.58
„ mono-metatoluylltartrate .....	+30.06	+13.59
„ mon-orthotoluylltartrate .....	+12.43	+11.82

Thus only in the case of the ortho-compound is the change of rotation over the experimental range of concentration such as to give approximately the real rotation of the pure substance on calculating for a concentration of 100 per cent., whilst in the other three cases the calculated figure is greatly in excess of the experimental value obtained with the pure substance in the liquid state.

*Rotation of Diethylic Mono-benzoyltartrate in Benzene Solution.*

Weight of solution. Grams.	Weight of substance. Grams.	Grams substance in 100 grams solution.	Density of solution at temp. of observa- tion of rotation.	Temp. of observa- tion of rotation.	Length of polari- meter tube.	$\alpha_D$ .	$[\alpha]_D$ .
5.0698	0.3812	7.519	0.8929	23.5°	1.0045	+0.725°	+10.75°
4.6773	0.4724	10.10	0.9033	20	1.0045	+0.762	+8.31

Thus in benzene solution the rotation is not only less than in the fused state, but even distinctly inferior to that exhibited in glacial

acetic acid solution. In benzene solution, association is much more probable than in glacial acetic acid, so that in the case of diethylic mono-benzoyltartrate, association would appear to be attended with diminished rotatory power, hence the high rotation of this compound in the pure state cannot be attributable to association.

*Molecular Volume of the Compounds.*

We have also endeavoured to ascertain whether the views of I. Traube concerning the relations between molecular volume and molecular weight are capable of throwing any light on the question of molecular aggregation in the case of these compounds. According to Traube, the molecular volume of a substance can be calculated from a knowledge of its molecular formula and constitution, the molecular volume being the sum of the atomic volumes of the constituent atoms together with a *co volume* which is constant for all individual molecules at a given temperature, and consequently a lower experimental molecular volume than the calculated would point to aggregation. In the following table we have recorded the experimental molecular volumes and the corresponding values calculated by Traube's formula for the several monacidyl substituted tartrates to which reference has been made in this paper, as well as for the corresponding diacidyl compounds of the ethylic and methylic series previously prepared by one of us.

*Molecular Volumes at 15°.*

		Experimental Mol. wt. $\frac{d}{d\ 15^\circ} = \text{Mol. vol.}$
Calculated.		
Ethylic monobenzoyltartrate .....	248.8	$\frac{310}{1.2127} = 255.6$
„ mono-paratoluyltartrate .....	264.9	$\frac{324}{1.1763} = 275.4$
„ mono-metatoluyltartrate ...	„	$\frac{324}{1.1794} = 274.7$
„ mono-orthotoluyltartrate ...	„	$\frac{324}{1.1933} = 271.5$
Ethylic dibenzoyltartrate .....	327.2	$\frac{414}{1.2018} = 344.5$
„ di-paratoluyltartrate .....	359.4	$\frac{442}{1.1643} = 379.6$
„ di-metatoluyltartrate .....	„	$\frac{442}{1.1661} = 379.0$
„ di-orthotoluyltartrate .....	„	$\frac{442}{1.1821} = 373.9$
Methylic dibenzoyltartrate .....	295.0	$\frac{386}{1.2554} = 307.5$

	Calculated.	Experimental Mol. wt. $\div$ $d_{15}^{\circ}$ = Mol. vol.
Methylic di-paratoluylltartrate.....	327.2	$\frac{414}{1.2126} = 341.4$
„ di-metatoluylltartrate ... „	„	$\frac{414}{1.2115} = 341.7$
„ di-orthotoluylltartrate .....	„	$\frac{414}{1.2329} = 335.8$
Methylic tartrate .....	138.2	$\frac{178}{1.3333} = 133.5$
Ethylic tartrate .....	170.4	$\frac{206}{1.2108} = 170.1$

In calculating the above molecular volumes, the following formula has been employed.

$$V_m = m10C + n3.05H + p1O' + q4O'' + r6O''' + 25.7$$

in which  $O'$  = atomic volume of hydroxylic oxygen  $\left\{ \begin{array}{l} m, n, p, q, \text{ and } r \\ = \text{the number of} \\ \text{atoms of the re-} \\ \text{spective elements} \\ \text{present in the} \\ \text{molecule.} \end{array} \right.$   
 $O'' =$  „ „ carbonylic „  
 $O''' =$  „ „ ether or ester „

25.7 = "Covolume" or molecular constant, further, 12.8 has been deducted for each benzene-ring present in the molecule (I. Traube, *Ber.*, 28, 413).

From the above figures it will be seen that the experimental molecular volumes of all these mon-acidyl and di-acidyl compounds are considerably in excess of those calculated by Traube's formula. This is not improbably due to the large number of atoms of oxygen contained in the molecules of these compounds and the very variable value of the atomic volume of this element, whilst the high molecular weight of course multiplies any error there may be in the atomic volumes used. Also, since the results for the diacidyl are less in harmony with the calculated figures than those for the monacidyl compounds, there is not improbably some error in the constant deducted for a benzene ring. It is, therefore, not possible to draw any further conclusions from these figures than that they do not point to association. It is, however, worthy of note that in the three series of isomeric toluyll compounds, the ortho-compound has in each case distinctly the lowest experimental molecular volume and the lowest rotation, whilst the para- and meta-compounds have almost identical molecular volumes (in two cases the para- has the higher and in the third the lower), although in all three cases the para- has a decidedly higher rotation than the meta-compound. On the other hand, the

calculated and experimental values for ethylic tartrate are almost identical, whilst the experimental molecular volume of methylic tartrate points to considerable association.

The results which we have arrived at may be summarised as follows.

1. The mono-benzoyl and three mono-toluyll substitution compounds of ethylic tartrate are all dextrorotatory like the ethylic tartrate from which they are derived.

2. At low temperatures, the dextrorotation is in all cases greater than that of ethylic tartrate, whilst already at  $100^{\circ}$  the dextrorotation of ethylic tartrate exceeds that of both the ortho- and the meta-toluyll compounds.

3. In the fused state, the mono-benzoyl compound has the highest and the mon-orthotoluyll compound the lowest dextrorotation, the paratoluyll has a higher rotation than the metatoluyll compound.

4. In glacial acetic acid solution, the rotation is in all cases very considerably lower than in the fused state, but the order of the rotatory powers is only in so far changed that the rotation of the mono-paratoluyll is greater than that of the mono-benzoyl compound. The rotation of the monobenzoyl compound in benzene is still lower than in acetic acid, and as association is more probable in benzene than in acetic acid, it follows that the high rotation of the fused monobenzoyl compound itself cannot be due to association.

5. The molecular weights determined by the cryoscopic method in glacial acetic acid solution are in all cases approximately normal.

6. The rotation of all the compounds is affected by temperature, increase of temperature being attended in every case with diminution of the dextrorotation. The rotation of the mono-benzoyl and mono-paratoluyll compounds is more sensitive to temperature than that of the meta-toluyll and ortho-toluyll compounds.

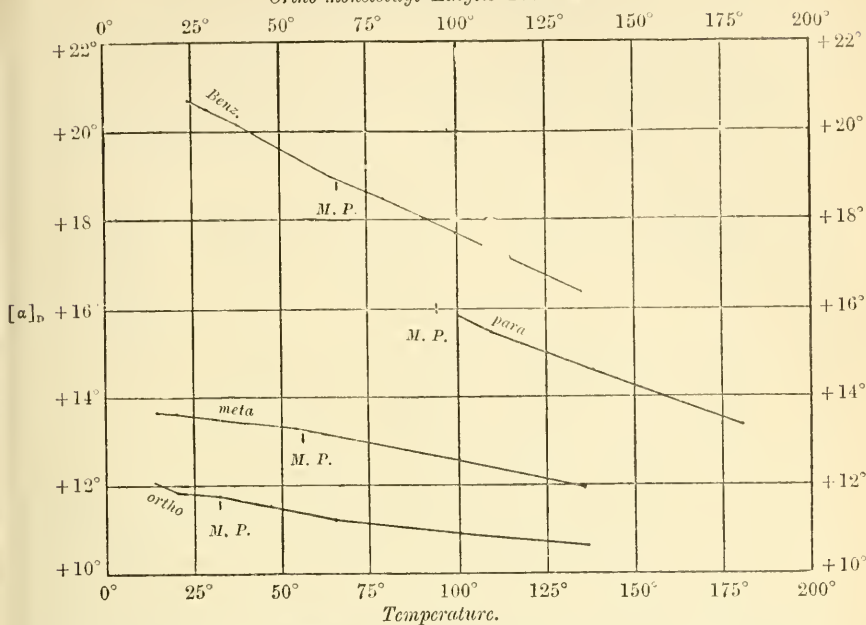
7. The change in rotation effected by a given change of temperature is much less in the case of these mon-acidyl than in that of the corresponding di-acidyl compounds of tartaric acid, but the absolute rotation of the mon-acidyl compounds is also much inferior to that of the corresponding di-acidyl compounds, and in proportion to their absolute rotation the temperature sensitiveness of the mon-acidyl is not very different and in some cases actually greater than that of the corresponding di-acidyl compounds.

8. Increase of temperature raises the dextrorotation of methylic and ethylic tartrates, it diminishes the levorotation of the di-benzoyl and di-toluyll derivatives, whilst it diminishes the dextrorotation of the mono-benzoyl and mono-toluyll derivatives of ethylic tartrate.

The levorotation of the di-acidyltartrates in question is conditioned by the aromatic groups, and similarly the high dextrorotation of the

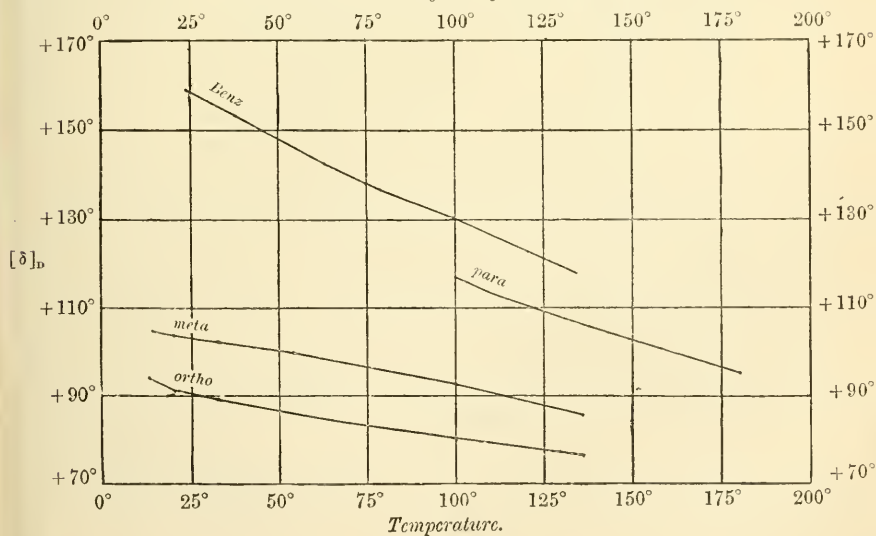


FIG. 1.—Influence of Temperature on the Specific Rotation of Monobenzoyl-, Para-, Meta-, and Ortho-monotoluyll Ethylic Tartrates.



The melting points of the compounds are indicated in the diagram by the position of the letters "M. P."

FIG. 2.—Influence of Temperature on Molecular Deviation of Monobenzoyl-, Para-, Meta-, and Ortho-monotoluyll Ethylic Tartrates.





mon-acidyltartrates is conditioned by the single aromatic group; in both cases, therefore, the influence of the aromatic groups diminishes as the temperature rises.

9. The mon-acidyltartrates melt at temperatures which are in remarkable proximity to the melting points of the corresponding di-acidyltartrates in all cases in which the latter have been obtained in the solid state, thus

*Melting Points.*

Methylic tartrate. 48°	Dibenzoyl- tartrate. 135·5°	Di- <i>p</i> -toluyl- tartrate. 88·5°	Di- <i>m</i> -toluyl- tartrate. 83°	Di- <i>o</i> -toluyl- tartrate. 56°
Ethylic tartrate. liquid.	62·5°	92—93°	liquid.	liquid.
	Monobenzoyl- tartrate. 66·0—66·5°	Mono- <i>p</i> -toluyl- tartrate. 94°	Mono- <i>m</i> -toluyl- tartrate. 56°	Mono- <i>o</i> -toluyl- tartrate. 32·5°

10. The rotatory power of the three isomeric mono-toluyltartrates follows the order of their molecular volumes, the same relationship holds good in the case of the three ethylic di-toluyltartrates, whilst in the case of the three methylic di-toluyltartrates the meta- has a very slightly greater molecular volume than the para-compound, although the rotatory power of the latter is much higher than that of the former.

11. The rotatory power of these mono-benzoyl- and mono-toluyltartrates is very similar in magnitude to that of the corresponding mono-chloracetyltartrates, approaching identity in the following cases.

Ethylic mono-trichloracetyltartrate .....	$[\alpha]_D^{68.5} = +17.53^\circ$
„ mono-benzoyltartrate .....	$[\alpha]_D^{99.5} = +17.69$
„ mono-monochloracetyltartrate.....	$[\alpha]_D^{99.3} = +17.32$
„ mono-monochloracetyltartrate.....	$[\alpha]_D^{20} = +11.44$
„ mono-orthotoluyltartrate .....	$[\alpha]_D^{20} = +11.82$

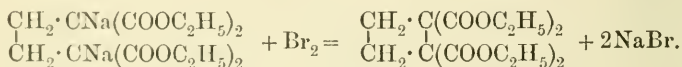
Whilst, however, the dextrorotation of the mono-chloracetyltartrates increases with the temperature, that of the mono-benzoyl- and mono-toluyltartrates diminishes under the same influence.

12. The molecular volumes of all the mon-acidyl- and di-acidyltartrates with aromatic acid radicles are in excess of the values calculated by Traube's formula, and would thus appear not to be associated. On the other hand, the molecular volume of ethylic tartrate is almost identical with the calculated value, whilst the molecular volume of methylic tartrate points to considerable association, the experimental being very distinctly inferior to the calculated molecular volume.

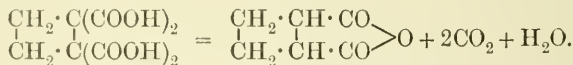
XXXII.—*Cis- and trans-Tetramethylene-(1 : 3)-dicarboxylic Acids and the Condensation of Formaldehyde with Ethylic Malonate.*

By E. HAWORTH and W. H. PERKIN, JUNR.

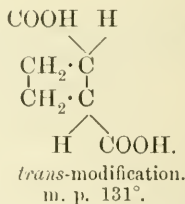
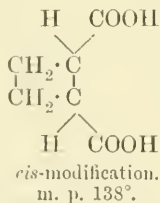
IN a communication made to this Society some time since by one of us (Trans., 1890, 57, 18), it was shown that the disodium compound of ethylic butanetetracarboxylate is readily acted on by bromine with the formation of ethylic tetramethylenetetracarboxylate,



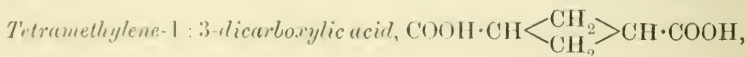
From this ethereal salt, by hydrolysis and elimination of two mols. of  $\text{CO}_2$  at  $200^\circ$ , the anhydride of tetramethylene-1 : 2-dicarboxylic acid is formed thus.



A subsequent very careful examination of this synthesis (Trans., 1894, 65, 572) enabled us to show that the tetramethylenedicarboxylic acid (1 : 2) formed in this way was, like hexahydrophthalic acid, capable of existing in well-defined *cis*- and *trans*-modifications, which may be represented by the formulæ,



The *cis*-acid readily yields an anhydride (melting at  $32^\circ$ ), but it was not found possible to prepare an anhydride of the *trans*-acid; if however, the *trans*-acid is distilled, it yields the anhydride of the *cis*-acid, and, *vice versa*, the *cis*-acid is completely converted into the *trans*-acid by heating with hydrochloric acid at  $180^\circ$ . It is evident from this method of formation that these acids are tetramethylenedicarboxylic acids, and their properties clearly prove that their isomerism is due to stereochemical grounds, and not to a difference in chemical structure.



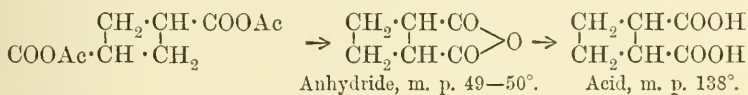
isomeric with the above acids, was first obtained by Markownikoff and Krestownikoff (*Annalen*, 1881, 208, 333) by the hydrolysis of the ethereal salt which is formed when ethylic  $\alpha$ -chloropropionate is heated with dry sodium ethoxide.



This beautifully crystalline substance, which was called paratetrylene-dicarboxylic acid, melts at  $170-171^\circ$ , and yields a double anhydride,  $\text{C}_4\text{H}_6(\text{CO} \cdot \text{C}_2\text{H}_3\text{O})_2$ , when its silver salt is treated with acetyl chloride.

When this anhydride is distilled, it undergoes an interesting change, and the distillate is found to consist of a new anhydride,  $\text{C}_4\text{H}_6 \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{CO} \end{smallmatrix} \text{O}$ , which, when pure, melts at  $49-50^\circ$ , and on treatment with water yields a dibasic acid,  $\text{C}_4\text{H}_6(\text{COOH})_2$ , melting at  $138^\circ$ .

Markownikoff supposes that these changes take place in the following way.



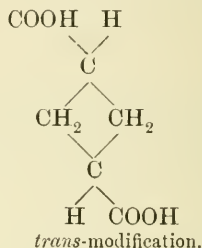
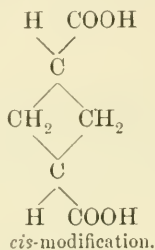
That is to say, he assumes that the tetramethylene-1:3-dicarboxylic acid, which is a derivative of glutaric acid, has during this process undergone molecular change, and become converted into 1:2-tetramethylenedicarboxylic acid, called by him orthotetrylenedicarboxylic acid, which is a derivative of succinic acid. It is extremely improbable that such simple reactions would bring about such a fundamental change of composition, and Markownikoff's interpretation is clearly shown to be incorrect when the substances which he assumes to have the formulæ  $\begin{array}{c} \text{CH}_2 \cdot \text{CH} \cdot \text{CO} \\ | \quad | \\ \text{CH}_2 \cdot \text{CH} \cdot \text{CO} \end{array} \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{O} \end{smallmatrix}$  and  $\begin{array}{c} \text{CH}_2 \cdot \text{CH} \cdot \text{COOH} \\ | \quad | \\ \text{CH}_2 \cdot \text{CH} \cdot \text{COOH} \end{array}$  are directly compared with the compounds having these constitutions which were obtained by us in the way described at the commencement of this paper. Thus, for example, although both the acids melt at  $138^\circ$ , the anhydride of *cis*-tetramethylene-1:2-dicarboxylic acid melts at  $32^\circ$ , whereas the melting point of the anhydride of Markownikoff's acid is  $49-50^\circ$ , and there are many other ways in which the acids differ, as will be shown in detail in this paper.

In Beilstein's *Handbuch* (vol. I., pp. 717-718) both *cis*-tetramethylene-1:2-dicarboxylic acid and Markownikoff's acid melting at  $138^\circ$  are represented as having the same formula, in spite of their being different substances, and as this has caused considerable confusion in the chemistry of the tetramethylene compounds, we decided to



investigate Markownikoff's acid with a view of determining its nature.

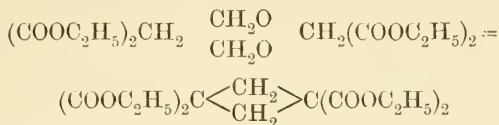
If we examine the formula of tetramethylene-1 : 3-dicarboxylic acid, it is at once apparent that this acid, like the corresponding (1 : 2) acid, should be capable of existing in the following two stereoisomeric forms.



and by repeating Markownikoff's work and also by means of new data, we have, as we think, been able to show conclusively that the isomerism of the ortho- and para-tetrylenedicarboxylic acids is simply due to the fact that they are the *cis*- and *trans*-modifications of 1 : 3-tetramethylenedicarboxylic acid. We found, in the first place, that the ethereal salt formed by the action of sodium ethoxide on ethylic chloropropionate, on hydrolysis, gives not only paratetrylenedicarboxylic acid melting at 171°, but also an acid melting at 133—135°, which, on examination, proved to be identical with orthotetrylenedicarboxylic acid, and the presence of which, in the product of hydrolysis, seems to have been overlooked by Markownikoff. This is strong evidence in favour of the acids being stereoisomeric, as it is quite usual to find the *cis*- and *trans*-forms produced together in such synthetical experiments as those described above. Then, again, the properties of the two acids are such as are commonly shown by stereoisomeric substances. Thus, paratetrylenedicarboxylic acid, like *trans*-1 : 2-tetramethylenedicarboxylic acid, does not yield an anhydride, but on distillation it yields the anhydride of orthotetrylenedicarboxylic acid, just as *trans*-1 : 2-tetramethylenedicarboxylic acid, on distillation, is converted into the anhydride of the *cis*-acid. The reverse change, that is, the conversion of ortho- into para-tetrylene acid by heating with hydrochloric acid at 180°, we have, so far, not been able to accomplish, since, under these conditions, further decomposition of the product evidently occurs with formation of syrupy acids which we have not further investigated.

During the course of this research, we were led to again investigate the condensation of formaldehyde with ethylic malonate, in the hope that in this way a method might be devised by which the tetrylenic acids could be obtained with much less labour and in much better yield

than is the case when Markownikoff's method is employed. It was conceivable that 2 mols. of formaldehyde might readily condense with 2 mols. of ethylic malonate according to the scheme

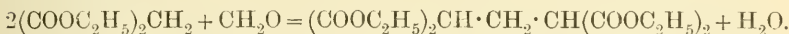


yielding ethylic tetramethylene-1:1:3:3-tetracarboxylate. From this ethereal salt, by hydrolysis and elimination of 2 mols.  $\text{CO}_2$ , the tetrylenic acids would be produced thus

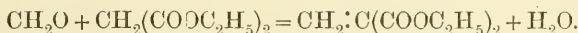


and, as will be shown later, it was actually found that the action does to some extent proceed in this way, but unfortunately the yield of tetrylenic acid, thus obtained, is only very small.

The condensation of ethylic malonate with formaldehyde was first investigated by one of us in 1886 (*Perkin, Ber.*, 19, 1053), acetic anhydride being employed as the dehydrating agent, and it was then shown that the principal product of the reaction was *ethylic propane-tetracarboxylate*,



It was, however, mentioned that a small quantity of an oil, boiling at  $208-212^\circ$ , was also isolated, which on analysis gave numbers agreeing with those required by *ethylic methylenemalonate*, a substance which might easily have resulted from the condensation of 1 mol. of ethylic malonate with 1 mol. of formaldehyde according to the equation



In 1894 (*Ber.*, 27, 2345), Knoevenagel published the results of an investigation on the condensation of ethylic malonate with formaldehyde in the presence of diethylamine as the condensing agent; in this way he obtained a good yield of ethylic propanetetracarboxylate which he converted into glutaric acid by hydrolysis and elimination of 2 mols.  $\text{CO}_2$ . Knoevenagel makes no mention of any previous paper on the subject, and appears to be ignorant of the fact that practically the whole of his results, including the preparation of glutaric acid, had been described in detail eight years previously (*Perkin, loc. cit.*).

In a long course of experiments which we have made in connection with this research on the condensation of formaldehyde with ethylic malonate, we have usually employed diethylamine instead of acetic

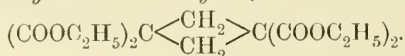
anhydride as the condensing agent, as it is more convenient and appears to lead to the same products. We find that, under the conditions described in this paper, the product of the reaction is a complicated mixture containing

*Ethyl methylenemalonate*,  $(\text{COOC}_2\text{H}_5)_2\text{C}:\text{CH}_2$ ,

*Ethyl propanetetracarboxylate*,



*Ethyl tetramethylenetetracarboxylate*,



and other substances of higher boiling point which are at present under investigation.

*Ethyl methylenemalonate* was isolated from the product of the reaction in the form of a polymeride which resembles white wax in appearance, and melts at about  $150^\circ$ ; this modification we have named ethyl paramethylenemalonate.

This remarkable substance, on distillation, is decomposed into an oil boiling constantly at  $208\text{--}210^\circ$ , and into very interesting higher boiling products which are at present under investigation. The numbers obtained in the analysis of the oil boiling at  $208\text{--}210^\circ$  agree exactly with those required for ethyl methylenemalonate,  $(\text{COOC}_2\text{H}_5)_2\text{C}:\text{CH}_2$ , and the fact that it boils only a few degrees higher than ethyl malonate (b. p.  $198^\circ$ ), proves that it must have this simple composition. If the oil, directly after distillation, is dissolved in chloroform and the well-cooled solution treated with bromine, the halogen is instantaneously absorbed with formation of ethyl  $\alpha\beta$ -dibromethane- $\alpha\alpha$ -dicarboxylate,  $(\text{COOC}_2\text{H}_5)_2\text{CBr}\cdot\text{CH}_2\text{Br}$ .

If, however, the fraction  $208\text{--}210^\circ$  is allowed to stand for 24 hours, at first sight no change appears to have taken place, but on closer examination it is seen that the oil has become converted into a hard and perfectly transparent polymeride, which melts, although not sharply, at a very high temperature and is quite different from the para-polymeride; this modification we have named ethyl metamethylenemalonate.\*

We have no doubt that the substance boiling at  $208\text{--}212^\circ$ , which was described and analysed in the first research on this subject (*loc. cit.*, p. 1054), was ethyl methylenemalonate. The fact that it polymerised on standing in the way it does was at the time overlooked.

Ethyl paramethylenemalonate behaves in a remarkable way when

\* For want of a better system of nomenclature, we have used the prefixes *para* and *meta* here in the same sense as they are used in paraldehyde and metaldehyde, and it appears to us that in doing so there is very little danger of these names being confused with para- and meta-compounds in the aromatic series.

hydrolysed with alcoholic potash, as under these conditions it yields *cis*-tetramethylene-1:3-dicarboxylic acid, but it is nevertheless not the ethereal salt of this acid, since this substance, which we obtained in quantity by the action of sodium ethoxide on ethylic chloropropionate, is a colourless oil which distils without decomposition and shows no signs of polymerising. During the course of our experiments on the polymeric forms of ethylic methylenemalonate, many attempts were made to determine the molecular weights of these polymerides by means of the cryoscopic method, using acetic acid as a solvent; but the results obtained were most unsatisfactory, and the same want of success attended all our attempts to determine the vapour density of the polymerides in a vacuum.

The ethylic paramethylenemalonate described in this paper is probably identical with a polymeric form of ethylic methylenemalonate, which Zelinsky (*Ber.*, 1889, 22, 3294) obtained by the action of methylene iodide on the sodium derivative of ethylic malonate, and which he describes as having properties like paraffin wax and melting at 155—156°. The molecular weight of this substance, which Zelinsky determined in acetic acid solution by the cryoscopic method, gave results agreeing closely with those required by the formula  $[(\text{COOC}_2\text{H}_5)_2\text{C}:\text{CH}_2]_2$ , and this chemist noticed that the polymeride, on distillation, yielded an oil boiling between 120° and 210°, from which, by the action of bromine, he obtained a dibromide boiling at 185—190° (75—85 mm.), and having approximately the composition  $\text{C}_8\text{H}_{12}\text{Br}_2\text{O}_4$ , that is, that of ethylic dibromethanedicarboxylate.

When the product of the condensation of formaldehyde with ethylic malonate is distilled under reduced pressure, an oil is obtained boiling at 250—300° (40 mm.); that this oil contains ethylic 1:1:3:3-tetramethylenetetracarboxylate appears to us to be proved by the fact that, in hydrolysis, it yields an oily acid, from which, by treatment in the manner described in detail in the experimental part of this paper, *cis*-1:3-tetramethylenedicarboxylic acid was isolated in quantity sufficient for analysis and identification.

Besides ethylic tetramethylenetetracarboxylate, there are other substances of interest produced during the condensation of formaldehyde with ethylic malonate; these are at present under examination, and we are also engaged in an investigation of the products formed when methylene iodide acts on the disodium compound of ethylic propanetetracarboxylate.

*Action of Sodium Ethylate on Ethylic  $\alpha$ -Chloropropionate. Formation of Cis- and Trans-Tetramethylene-1:3-dicarboxylic Acids.*

In our first experiments on this reaction, we followed closely the method given by Markownikoff (*Annalen*, 1881, 208, 334); subsequently, however, we introduced some modifications of importance, which enabled us to prove that the product of the reaction contained the ethylic salts of both the *cis*- and *trans*-tetramethylenedicarboxylic acids, and not only that of the latter, as Markownikoff seems to indicate.

Ethylic  $\alpha$ -chloropropionate (45 grams) was heated in an oil bath to about 60–70° in a flask which was connected by means of a cork and bent tube to a small condenser; and dry\* sodium ethoxide (containing 7.5 grams of sodium) was added in small quantities at a time, a stream of dry hydrogen being passed continuously through the apparatus during the operation. As each small quantity of sodium ethoxide was added, a vigorous action took place, the temperature rising to the point of ebullition, but the process was carefully regulated so that only traces of ethylic chloropropionate distilled over. During the progress of the decomposition, it was found advantageous to raise the temperature of the oil bath once or twice to 100° for a short time, in order to drive off as much as possible of the alcohol which had been formed during the reaction.

After all the sodium ethylate had been added, the temperature was kept at 100° for about half an hour; the mixture was then cooled, decomposed by dilute sulphuric acid, and the oily products extracted with ether. The ethereal solution, washed with sodium carbonate solution and with water, was dried over calcium chloride and evaporated, and the dark brown, oily residue distilled under the ordinary pressure until the temperature rose to 200°. The residue was then distilled under reduced pressure, and after two fractionations a good deal of oil was obtained boiling between 173° and 178° (110 mm.).

The yield of this oil, which on examination was found to consist of the mixed ethylic salts of *cis*- and *trans*-tetramethylenedicarboxylic acids, was only 10 per cent. of the ethylic chloropropionate employed, and this led us to make experiments on the action of sodium ethoxide on ethylic  $\alpha$ -bromopropionate, as it seemed likely that the decomposition would take place more readily in this case. The results of these experiments showed, however, that although the reaction proceeded in the same way, the yield of ethylic tetramethylenedicarboxylate was even less than in the case of the ethylic chloro-

\* This was freed as far as possible from alcohol by heating at 200° in a stream of dry hydrogen.



propionate, the actual amount obtained being never more than 5 per cent. of the ethylic bromopropionate employed.

The crude ethylic tetramethylenedicarboxylate, boiling at 173—178° (110 mm.), was dissolved in methylic alcohol and hydrolysed by boiling with potash in a reflux apparatus for 2 hours; the dark-coloured product was then mixed with water, and the solution evaporated on the water bath, with the frequent addition of small quantities of water, until every trace of methylic alcohol had been removed.

The concentrated solution, acidified with hydrochloric acid, was extracted many times with pure ether; and the ethereal solution of the mixed acids, after being dried over calcium chloride, was filtered and evaporated, and the oily residue placed over sulphuric acid in a vacuum desiccator. As this residue, even on long standing, only partially crystallised, it was dissolved in a little water and the solution saturated with hydrogen chloride, when crystals gradually separated. These were collected, washed with hydrochloric acid, and dried at 100°; they then melted at 166—169°, but on subsequently recrystallising from hydrochloric acid, the melting point rose to 170—171°. This beautiful, colourless, crystalline acid gave the following results on analysis.

0.1490 gave 0.2720 CO<sub>2</sub> and 0.0736 H<sub>2</sub>O. C = 49.79; H = 5.49.

C<sub>4</sub>H<sub>6</sub>(COOH)<sub>2</sub> requires C = 50.00; H = 5.55 per cent.

This acid is *trans-tetramethylene-1:3-dicarboxylic acid*, identical with the acid of the same melting point obtained by Markownikoff, and called by him paratetrylenedicarboxylic acid or homoitaconic acid.

*Cis-tetramethylenedicarboxylic acid*, COOH·CH< $\begin{smallmatrix} \text{CH}_2 \\ \text{CH}_2 \end{smallmatrix}$ >CH·COOH.

So far as we have been able to discover, Markownikoff did not examine the mother liquors from the crystallisation of *trans-tetramethylenedicarboxylic acid* (see previous section); as, however, it seemed probable that these might contain the *cis*-acid, we subjected them to careful investigation. The combined hydrochloric acid liquors from a long series of experiments were filtered, evaporated to a small bulk on the water bath, and the residue placed over solid potash in a vacuum; after some time, crystals began to form, and during some months these gradually increased until the whole had assumed a pasty consistency. The mass, spread on porous porcelain, was left for some weeks until the mother liquor had been entirely absorbed, and the crystals were then dissolved in water, the solution boiled with pure animal charcoal, filtered, and saturated with gaseous hydrogen chloride. As the solution did not deposit crystals on standing, it was

placed over solid potash in a vacuum desiccator and allowed to concentrate gradually when after some days crystals separated, which were collected and drained on porous porcelain. As these crystals, dried at  $100^{\circ}$ , melted not very sharply at  $128\text{--}133^{\circ}$ , they were recrystallised, the operation being carried out exactly as before, except that the first few crystals, which it was thought might contain traces of the *trans*-acid, were neglected.

In this way, colourless crystals were obtained which melted at  $129\text{--}133^{\circ}$ , and on analysis gave the following numbers.

0.1380 gave 0.2497  $\text{CO}_2$  and 0.0704  $\text{H}_2\text{O}$ .  $\text{C} = 49.34$ ;  $\text{H} = 5.67$ .

$\text{C}_4\text{H}_6(\text{COOH})_2$  requires  $\text{C} = 50.0$ ;  $\text{H} = 5.55$  per cent.

Although the melting point of this acid was somewhat low, the examination of its properties clearly indicated that it was *cis*-tetramethylenedicarboxylic acid, which, according to Markownikoff, when perfectly pure melts at  $138\text{--}139^{\circ}$ . In order to be quite sure of this identity, the acid was digested for half an hour with excess of acetyl chloride, and the solution allowed to evaporate slowly over potash; the mass of beautiful, needle-shaped crystals thus obtained, after being drained on a plate, melted at  $50\text{--}51^{\circ}$ , and consisted of pure *cis*-tetramethylenedicarboxylic anhydride.

0.1210 gave 0.2529  $\text{CO}_2$  and 0.0534  $\text{H}_2\text{O}$ .  $\text{C} = 57.01$ ;  $\text{H} = 4.90$ .

$\text{C}_4\text{H}_6(\text{C}_2\text{O}_3)_2$  requires  $\text{C} = 57.14$ ;  $\text{H} = 4.76$  per cent.

This anhydride was reconverted into the acid, which then melted at  $135\text{--}136^{\circ}$ .

#### *Action of Acetic Anhydride on trans-Tetramethylene-1 : 3-dicarboxylic Acid.*

Two experiments on the action of acetic anhydride on *trans*-tetramethylene-1 : 3-dicarboxylic acid were made, with the following results.

(1) Two grams of the pure acid were warmed with a large excess of acetic anhydride until it just dissolved. The solution was then placed in a desiccator containing caustic potash and allowed to evaporate in a vacuum.

(2) A similar solution of the acid in acetic anhydride was boiled in a reflux apparatus for 6 hours, and the solution then evaporated over caustic potash in a vacuum.

The product of both experiments was a thick syrup, which only showed signs of crystallising after being kept for several weeks. Both products had the same composition, and consisted of a double anhydride of acetic and *trans*-tetramethylenedicarboxylic acids, as is shown by the following analyses and experiments.

- (1) 0.1456 gave 0.0697  $\text{H}_2\text{O}$  and 0.2807  $\text{CO}_2$ .  $\text{C} = 52.58$ ;  $\text{H} = 5.32$ .  
 (2) 0.1500 „ 0.0730  $\text{H}_2\text{O}$  „ 0.2895  $\text{CO}_2$ .  $\text{C} = 52.64$ ;  $\text{H} = 5.40$ .  
 $\text{C}_4\text{H}_6(\text{CO}_2\cdot\text{C}_2\text{H}_3\text{O})_2$  requires  $\text{C} = 52.63$ ;  $\text{H} = 5.26$  per cent.

Both products dissolved in boiling water, and on cooling the solutions, crystals of *trans*-tetramethylenedicarboxylic acid melting between  $170^\circ$  and  $171^\circ$  were deposited. The presence of the acetyl groups was proved in the following manner. The syrup was warmed with a solution of sodium carbonate, and the liquid, after being acidified with dilute sulphuric acid, was submitted to steam distillation until the distillate was no longer acid. The distillate, when neutralised with barium carbonate, gave a red coloration with ferric chloride, changing to a brown precipitate on boiling. The solution of the barium salt was concentrated, and the sparingly soluble silver salt obtained from it was analysed, when it gave numbers corresponding with those required for silver acetate,  $\text{CH}_3\cdot\text{COOAg}$ .

Found  $\text{C} = 14.19$ ;  $\text{H} = 1.97$ ;  $\text{Ag} 64.59$ .

Theory  $\text{C} = 14.37$ ;  $\text{H} = 1.79$ ;  $\text{Ag} 64.66$  per cent.

The results of these experiments confirm Markownikoff's statement that *trans*-tetramethylenedicarboxylic acid (paratetrylenedicarboxylic acid) is converted into a double anhydride,  $\text{C}_4\text{H}_6(\text{CO}_2\text{C}_2\text{H}_3\text{O})_2$ , when its silver salt is treated with acetyl chloride.

### *Condensation of Formaldehyde with Ethylic Malonate.*

As was mentioned in the introduction, the condensation of formaldehyde with ethylic malonate was first investigated by one of us in 1886 (*Ber.*, 19, 1053), with the result that, besides ethylic propanetetracarboxylate,  $(\text{COOC}_2\text{H}_5)_2\cdot\text{CH}\cdot\text{CH}_2\cdot\text{CH}(\text{COOC}_2\text{H}_5)_2$ , a small quantity of an oil was obtained which boiled at  $208\text{--}212^\circ$ , and on analysis gave numbers agreeing with the formula of ethylic methylenemalonate,  $\text{CH}_2\cdot\text{C}(\text{COOC}_2\text{H}_5)_2$ . It was stated at the time that the experiments were to be continued, and as we required ethylic propanetetracarboxylate for our synthetical work in the course of this research, we used the opportunity for investigating the condensation of formaldehyde and ethylic malonate in more detail than had previously been done.

In the first experiments, acetic anhydride was used as the condensing agent, but on this occasion we have usually employed diethylamine, as we found that this base, which has been recommended by Knoevenagel (*Ber.*, 1894, 27, 2345) for this purpose, is more convenient in working with large quantities.

Ethylic malonate (160 grams) is mixed with a 40 per cent. solution of formaldehyde (60 grams) and alcohol added until the solution becomes clear; the mixture is allowed to stand at the ordinary tempera-

ture for 12 hours, and then heated on the water bath for 2 hours in a reflux apparatus. After cooling, about three times the volume of ether is added, the ethereal solution washed first with a solution of sodium carbonate, then with water, dried over calcium chloride, the ether evaporated, and the residual oil repeatedly fractionated under reduced pressure, the fractions collected being the following.

I. 130—190° (70 mm.).

II. 210—230° (40 mm.).

III. 250—300° (40 mm.).

These were then further investigated as described in the following sections.

*Ethylic Methylenemalonate*,  $\text{CH}_2:\text{C}(\text{COOC}_2\text{H}_5)_2$ .

The oil obtained by the condensation of formaldehyde with ethylic malonate as described in the previous section, and boiling at 130—190° (70 mm.), was distilled under the ordinary pressure, when it showed the following behaviour. The liquid began to boil at 190°, and a small quantity of oil, consisting possibly of unchanged ethylic malonate, passed over between this and 200°; the temperature then rose rapidly to 205°, about half the oil distilling between this and 215°. As the remainder of the oil proved to have a very high boiling point, the distillation was continued under reduced pressure, and in this way large fractions were obtained boiling at 210—230° and 250—300° under a pressure of 40 mm.; these were added to the similar fractions obtained as described in the previous section. This behaviour appears to indicate that during distillation under the ordinary pressure condensation must take place between some of the constituents of the oil, and this was subsequently proved to be the case.

On standing for some days, the fraction boiling at 200—212°, under ordinary pressure, solidified almost completely to a hard, wax-like mass; this was ground up, left in contact with porous porcelain for some days, and then washed with light petroleum, in which it is insoluble, in order to remove any traces of oily impurity. The residue, which in appearance closely resembles paraffin wax, gave on analysis the following results.

0.1218 gave 0.2460  $\text{CO}_2$  and 0.0786  $\text{H}_2\text{O}$ . C = 55.08; H = 7.17.

0.1620 „ 0.3318  $\text{CO}_2$  „ 0.1000  $\text{H}_2\text{O}$ . C = 55.80; H = 6.86.

0.1456 „ 0.2980  $\text{CO}_2$  „ 0.0917  $\text{H}_2\text{O}$ . C = 55.82; H = 7.01.

$\text{CH}_2:\text{C}(\text{COOC}_2\text{H}_5)_2$  requires C = 55.81; H = 6.98 per cent.

This substance, which we propose to call *para*-ethylic methylenemalonate, is a polymeric form of ethylic methylenemalonate and evidently identical with the substance which Zelinsky (*Ber.*, 1889, 22, 3294) obtained by the action of methylene iodide on the sodium derivative of ethylic malonate.



When heated in a capillary tube, it begins to melt at about  $146^{\circ}$  and is completely melted at  $150^{\circ}$ , whilst at a somewhat higher temperature gas begins to be evolved, the decomposition being rapid at  $200^{\circ}$ . The polymeride is very sparingly soluble in alcohol, ether, light petroleum, and benzene, but dissolves moderately readily in warm acetic acid, and owing to this we made several attempts to determine its molecular weight by Raoult's method, but the results were very unsatisfactory, as, although in two experiments values were obtained which seemed to indicate that the substance had the formula  $2\text{CH}_2:\text{C}(\text{COOC}_2\text{H}_5)_2$ , the results were not constant, much higher values being obtained in some experiments than in others.

The polymeride of ethylic methylenemalonate prepared by Zelinsky, melted at  $155\text{--}156^{\circ}$  and had properties similar to those of the substance described above; in one experiment, using acetic acid as the solvent, Zelinsky obtained numbers for the depression of the freezing point which led him to conclude that the polymeride had the formula  $2\text{CH}_2:\text{C}(\text{COOC}_2\text{H}_5)_2$ , but when the insolubility of the substance and its general properties are taken into account it appears to us that it must have a very much higher molecular weight.

*Distillation of Para-Ethylic Methylenemalonate. Formation of Ethylic Methylenemalonate and its Meta-Polymeride.*

When heated cautiously in a small distillation flask with a naked flame, para-ethylic methylenemalonate first melts and then decomposes with effervescence and evolution of a vapour possessing a very pungent and penetrating smell, something like that of formaldehyde. On heating more strongly, distillation soon commences and nearly the whole passes over between  $205^{\circ}$  and  $250^{\circ}$  as a pale yellow oil, but a small quantity of an oil of higher boiling point and some carbonaceous matter remains in the distillation flask.

On refractioning the distillate, about one-fourth distilled between  $205^{\circ}$  and  $215^{\circ}$ , and from this, on again fractioning, a considerable quantity of a colourless, pungent oil passed over constantly at  $208\text{--}210^{\circ}$ .\* This, on analysis, gave the following numbers.

0.1601 gave  $0.3268\text{ CO}_2$  and  $0.1010\text{ H}_2\text{O}$ .  $\text{C} = 55.70$ ;  $\text{H} = 7.01$ .

$\text{CH}_2:\text{C}(\text{COOC}_2\text{H}_5)_2$  requires  $\text{C} = 55.81$ ;  $\text{H} = 6.98$  per cent.

As this oil boils at a temperature only slightly higher than ethylic malonate (b. p.  $198^{\circ}$ ), it is clear that it consists of ethylic methylenemalonate and is not a polymeride; this view is borne out by the

\* This oil is obviously identical with the substance (b. p.  $208\text{--}212^{\circ}$ ) previously isolated by one of us (*Ber.*, 1886, **19**, 1053) from the products of the condensation of ethylic malonate with formaldehyde in the presence of acetic anhydride; the analysis of this oil gave  $\text{C} = 55.40$ ;  $\text{H} = 7.31$  per cent.



general properties of the substance. It is readily soluble in the usual organic solvents and its solution in chloroform decolorises bromine without the evolution of hydrogen bromide. In order to investigate this action, about 1 gram of the pure substances was, directly after distillation, dissolved in chloroform, cooled well, and a solution of bromine in chloroform run in until the colour just remained permanent. The chloroform was then removed by passing a current of dry air, and the residual oil analysed with the following result.

0.2120 gave 0.2450 AgBr. Br = 49.19.

$C_5H_{12}Br_2O_4$  requires Br = 48.19 per cent.

These numbers agree sufficiently well to show that the ethylic methylenemalonate has, during this reaction, united with 2 atoms of bromine with formation of *ethylic  $\alpha\beta$ -dibromoethane- $\alpha\alpha$ -dicarboxylate*, and it is our intention to prepare this compound in larger quantities in order to examine its properties in detail.

When ethylic methylenemalonate boiling at 208–210° is kept, it rapidly polymerises, undergoing hardly any change in appearance, and in 24 hours it is completely converted into a hard, perfectly transparent polymeride, which is quite different in properties from the opaque, waxy-like *para*-ethylic methylenemalonate: for this new polymeride we propose the name *meta-ethylic methylenemalonate*.

This polymeride is very like horn in consistency, being very difficult to break, although it can be cut into shavings with a knife; it is very sparingly soluble in the usual solvents, and when heated in a capillary tube it sinters at about 225°, and between 240° and 250° the soft mass gives off gas and decomposes without any definite melting point being observable.

When a small piece is heated in a test tube, it becomes soft and gives off a pungent gas smelling like formaldehyde, the soft mass then suddenly melts and decomposes rapidly, nearly the whole distilling as a colourless oil, and leaving only a trace of carbonaceous residue. We propose to carefully investigate the products of high boiling point which are formed in the distillation of both the *para*- and *meta*-polymerides of ethylic methylenemalonate.

In his experiments on ethylic methylenemalonate, Zelinsky distilled the *para*-polymeride and obtained thus an oil boiling at 120–210° which he considered to contain ethylic methylenemalonate. By treating this fraction with bromine and subsequent distillation, he isolated an oil boiling at 185–190° (at 75–85 mm.) which, on analysis, gave numbers agreeing approximately with the formula  $CH_2Br \cdot CBr(COOC_2H_5)_2$ . Found Br = 43.67 and 43.99. Theory Br = 48.19 per cent.

*Action of Alcoholic Potash on Para-Ethylic Methylenemalonate. Formation of cis-Tetramethylene-1 : 3-dicarboxylic Acid.*

In order, if possible, to obtain some clue to the nature of para-ethylic methylenemalonate, its behaviour towards alcoholic potash was investigated.

Ten grams of the polymeride were added to a solution of 20 grams of potash dissolved in ethylic alcohol and the mixture boiled in a reflux apparatus for 2 hours; water was then added, the clear solution evaporated to dryness on a water bath, to remove all trace of alcohol, and the residue, dissolved in a little water, was acidified and extracted repeatedly with ether; the ethereal solution, dried over calcium chloride, was then evaporated, and the residue heated at  $180^{\circ}$  in a small retort. This experiment was carefully performed, with a view to determine whether any acrylic acid was produced in this way, but although much carbon dioxide was evolved, practically no acid distilled over during the operation even when the temperature was raised to  $220^{\circ}$ . It appears, therefore, that no methylenemalonic acid,  $\text{CH}_2\text{:C}(\text{COOH})_2$ , is formed during the hydrolysis of the polymeride with alcoholic potash, since this acid, if present, should have yielded acrylic acid on heating at  $220^{\circ}$ .

As soon as the evolution of carbon dioxide had ceased, the residue was dissolved in water, boiled with animal charcoal, filtered, and the concentrated solution allowed to evaporate over sulphuric acid in a vacuum. As no crystals were obtained in this way even after the whole of the water had evaporated, the residue was further purified by very rapidly distilling it under a pressure of 20 mm. On dissolving the colourless, oily distillate in a very little water, saturating the solution with hydrogen chloride, and allowing it to remain for a long time, colourless crystals were deposited, which were collected and further purified by recrystallisation from hydrochloric acid.

The analysis gave the following result.

0.1544 gave 0.2820  $\text{CO}_2$  and 0.0798  $\text{H}_2\text{O}$ . C = 49.81; H = 5.74.

$\text{C}_4\text{H}_6(\text{COOH})_2$  requires C = 50.00; H = 5.55 per cent.

This acid melted at  $131\text{--}132^{\circ}$  and showed all the properties of *cis-tetramethylene-1 : 3-dicarboxylic acid*; that it was really this acid was shown by converting it into its anhydride which was found to melt at  $50\text{--}51^{\circ}$ , the melting point of the anhydride of the *cis*-acid. The formation of tetramethylenedicarboxylic acid in this way might be taken as evidence that para-ethylic methylenemalonate was ethylic tetramethylenetetracarboxylate, but this is not the case, since the latter ethereal salt is a colourless liquid of quite different properties and shows no tendency to change into a wax-like polymeride.

*Examination of the Oil boiling at 250—300° (40 mm.) produced during the Condensation of Formaldehyde with Ethylic Malonate.*

In the examination of this oil, it was not found possible to obtain from it by fractional distillation a product of constant boiling point. It was therefore hydrolysed by boiling for 4 hours with an equal weight of pure potash dissolved in alcohol; the product was mixed with water, the solution evaporated until free from alcohol, acidified with hydrochloric acid, and repeatedly extracted with ether. Since, however, the ethereal solution on evaporation deposited only about one-tenth part of the acid which was to have been expected, the aqueous liquors were evaporated to dryness, and the powdered mass extracted with ether in a Soxhlet apparatus. In this way, the required amount of acid was ultimately obtained as a thick syrup, which, even when exposed for some days over sulphuric acid in a vacuum, showed no signs of solidifying. This crude product was heated at 200° in an oil bath until the evolution of carbon dioxide had ceased, and the residue converted into the ethereal salt by treatment with alcohol and sulphuric acid in the usual manner. The ethereal salt, after being well washed with dilute sodium carbonate and dried over calcium chloride, was repeatedly fractionated under reduced pressure; in this way, a considerable fraction was obtained, distilling constantly at 172° (105 mm.), and evidently consisting of nearly pure ethylic tetramethylene-1 : 3-dicarboxylate, the boiling point of which had previously been ascertained to be 173—178° (110 mm.).

This ethereal salt, on hydrolysis in the usual way (see p. 377), yielded a crystalline acid melting at about 130°, which, on analysis, gave the following results.

0.1889 gave 0.3470  $\text{CO}_2$  and 0.095  $\text{H}_2\text{O}$ .  $\text{C} = 50.1$ ;  $\text{H} = 5.59$ .

$\text{C}_4\text{H}_6(\text{COOH})_2$  requires  $\text{C} = 50.00$ ;  $\text{H} = 5.55$  per cent.

From this acid, the *silver salt* was obtained as a gelatinous precipitate in the usual manner by precipitating the neutral solution of the ammonium salt with silver nitrate. It gave the following results on analysis.

0.2058 gave 0.1500  $\text{CO}_2$ , 0.032  $\text{H}_2\text{O}$ , and 0.1242 Ag.  $\text{C} = 19.88$ ;  $\text{H} = 1.73$ ;  $\text{Ag} = 60.35$ .

$\text{C}_4\text{H}_6(\text{COOAg})_2$  requires  $\text{C} = 20.11$ ;  $\text{H} = 1.68$ ;  $\text{Ag} = 60.31$  per cent.

The molecular weight of the acid was determined in acetic acid solution by the cryoscopic method.

I. 0.132 gram of substance dissolved in 32.41 grams of acetic acid caused a depression of 0.11° in the melting point.

II. 0.1463 gram of substance dissolved in 32.41 grams of acetic acid caused a depression of  $0.115^{\circ}$  in the melting point.

Molecular weight found was I = 144 ; II = 153.

Calculated for  $C_6H_8O_4$  = 144.

The properties of this acid indicated that it was *cis*-tetramethylene-1:3-dicarboxylic acid, but in order to be sure of this, the remainder of the acid was converted into the anhydride which melted at  $50-51^{\circ}$ , and was in all respects identical with the anhydride of the *cis*-acid which had previously been obtained.

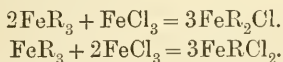
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MANCHESTER.

### XXXIII.—*Action of Ferric Chloride on Ethereal Salts of Ketone Acids.*

By ROBERT SELBY MORRELL, M.A., Ph.D., and JAMES MURRAY CROFTS, B.A., B.Sc.

THE colour reactions between ferric chloride and organic substances, especially di-ketones and ethereal salts of ketone acids, have been investigated by Claisen, Traube, and Wislicenus, but the compounds formed have not as yet been isolated. Claisen (*Annalen*, 1894, 281, 344) has observed that the red, crystalline ferriacetylacetone,  $Fe(C_5H_8O_2)_3$ , or ferribenzoylacetone,  $Fe(C_{10}H_{10}O_2)_3$ , dissolved in alcohol, gives a red solution, and on the addition of aqueous ferric chloride, a much deeper red coloration is produced, just as when aqueous ferric chloride is added to acetylacetone or benzoylacetone. A series of colour changes also occurs when alcoholic solutions of ferrioxymethylenecamphor are treated with aqueous ferric chloride.

The iron salts mentioned above are insoluble in water, but the alcoholic solutions, after treatment with ferric chloride, can be diluted with water to any extent, without separation of the insoluble iron salts. Claisen considers that the reaction with ferric chloride may be expressed by the following equations.



[R is the residue of acetylacetone or oxymethylenecamphor or benzoylacetone.]

The red or violet colorations which ferric chloride gives with alcoholic solutions of ketone ethereal salts may be due to the formation of soluble salts of the type  $FeR_2Cl$  or  $FeRCl_2$  (Claisen).

Claisen, Traube, and Wislicenus consider that the colour reaction



with ferric chloride indicates the existence of an enolic grouping in di-ketones and ethereal salts of di-ketone acids.

Traube (*Ber.*, 1896, 29, 1718) points out that the shade and intensity of the colour depends on the solvent used, strongly associated solvents, such as water, methylic alcohol, and ethylic alcohol, favouring the production of the enolic form, whilst in non-associated solvents, such as benzene, chloroform, and carbon tetrachloride, the aldo-form is much more stable.

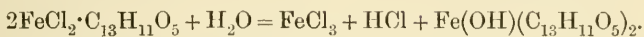
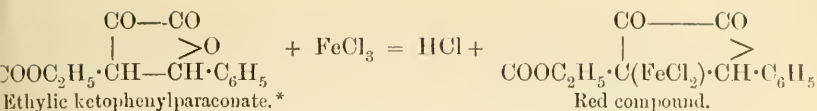
Knorr (*Ber.*, 1897, 30, 2387) has isolated five tautomeric ethylic di-acetylsuccinates, two of the forms giving the ferric chloride reaction, and being considered to contain enolic groupings in the anti-position. The keto-forms, in solution, pass into the enolic forms, and *vice versa*, until equilibrium is attained.

We noticed that when ethylic acetoacetate was added to a solution of anhydrous ferric chloride in dry ether, a deep violet oil separated. The production of a coloured oil was also observed in the case of ethylic methylacetoacetate, ethylic ethylacetoacetate, ethylic benzilidenedi-acetoacetate, ethylic oxalacetate, ethylic ketophenylparaconate, and the lactone of ethylic oxalocitrate. In the last three cases, the oils were of a deep red colour. By washing with dry benzene or dry ether, and removing the excess of the benzene or ether in a vacuum, the purple oil from ethylic benzilidenedi-acetoacetate and the red oil from ethylic ketophenylparaconate became solid. Only in these two instances have we as yet been able to obtain solids almost free from ferrous iron, and we are inclined to consider the red substance from ethylic ketophenylparaconate as a derivative of ferric chloride, one chlorine atom of the  $\text{FeCl}_3$  being replaced by the univalent residue of the ethereal salt, whilst the red oil from the lactone of ethylic oxalocitrate, may be regarded as an additive product of ferric chloride and the lactone salt.

The evidence in support of these views may be summarised as follows.

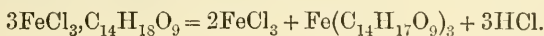
(a) The red solid from ethylic ketophenylparaconate is decomposed by excess of water into ferric chloride and a basic iron salt of ethylic ketophenylparaconate. The analysis of the red substance shows the presence of both chlorine and iron, nearly in the proportions required for  $\text{FeCl}_2 \cdot \text{C}_{12}\text{H}_{11}\text{O}_5$ ; the red colour is more stable in aqueous solution towards ether, and in ethereal solution towards chloroform, than in the case of the purple colorations, as when ferric chloride solution is added to ethylic acetoacetate, hydrochloric acid is produced in the reaction, without any oxidation by the ferric chloride occurring. The formation of the red compound from ethylic ketophenylparaconate, and its decomposition by water, may probably be expressed by the following equations,





The hydrochloric acid formed decomposes some of the red compound into ferric chloride and the original ethylic ketophenylparaconate.

(b) The red oil from ferric chloride and the lactone of ethylic oxalocitrate is either an additive product of ferric chloride with the lactone of the ethereal salt, or an  $\text{FeCl}_2\text{X}$  compound (where X is the acid radicle of the lactone of the ethereal salt). It does not contain the  $\text{FeX}_3$  salt, since it is insoluble in benzene, whilst the iron salt is easily soluble. Moreover, with water, it undergoes a similar decomposition to that in the case of the ketophenylparaconic substance, giving ferric chloride and the normal ferric salt of the organic acid. This decomposition may be expressed by the equation,



The formation of coloured oils with ethereal ferric chloride and the ethereal salts of ketonic acids may lead to the separation of the enolic from the ketonic forms. It is our intention to examine this, and to endeavour to isolate the tautomeric modifications.

## EXPERIMENTAL PART.

### *Action of Anhydrous Ferric Chloride on Ethylic Ketophenylparaconate.*

Ethylic ketophenylparaconate was prepared from benzaldehyde and ethylic oxalacetate (Wislicenus, *Ber.*, 1892, **25**, 3448), and recrystallised several times from alcohol. Ferric chloride, dissolved in dry ether, and ethylic ketophenylparaconate were mixed in exact molecular proportions, the red oil which separated was washed by decantation with anhydrous ether, and excess of the latter removed in a vacuum. Hydrochloric acid was given off, but no ferrous iron could be detected. After the removal of the acid in a vacuum over soda-lime, and the addition of more dry ether, a dark red, crystalline powder separated, which was washed on the filter with more dry ether and then dried in a vacuum. Analyses

	Oil freed from HCl in a vacuum.	Red powder.
Fe.....	15.56	15.28, 15.81.
Cl.....	19.5	21.8, 21.5, 19.55.

$\text{FeCl}_2 \cdot \text{C}_{13}\text{H}_{11}\text{O}_5$  requires Fe = 14.97 ; Cl = 19.0 per cent.

$\text{FeCl}_3 \cdot \text{C}_{13}\text{H}_{12}\text{O}_5$  „ Fe = 13.6 ; Cl = 25.94 „

\* Wislicenus and Hjensen (*Ber.*, **26**, 2144).

The red oil, if left for some weeks under dry ether, becomes crystalline (long rhombic needles). These crystals were washed with ether until the washings gave only a trace of iron and chlorine.

Melting point, 146—147° with decomposition. On analysis, it gave Fe = 13.29 ; Cl = 15.52 ; C = 41.9, 41.22, 39.4 ; H = 4.2, 4.19, 4.16.

This substance could not be purified further ; it is probably some of the  $\text{FeCl}_2\text{X}$  compound which has undergone decomposition.

*Action of Water on the Red Compound.*

Cold water removed 11 per cent. of iron and 21.4 per cent. of the chlorine, that is, all the chlorine, from the red powder. The dark red solid left was dried on a tile and added to hot methylic alcohol ; on rapidly filtering, an orange, crystalline substance was deposited, which could not be redissolved in the same solvent. The analysis showed it to be a basic ferric salt of ethylic ketophenylparaconate, identical with that obtained by the addition of aqueous ferric chloride to ethylic ketophenylparaconate dissolved in alcohol, and subsequently diluting with much water. Analysis.

	Fe.	C.	H.
I.	10.32	54.93	4.7.
II.	9.94	55.00	4.3.

$\text{Fe}(\text{OH})(\text{C}_{13}\text{H}_{11}\text{O}_5)$  requires Fe = 9.87 ; C = 55.0 ; H = 4.05 per cent.

The iron salt crystallises in aggregates of needles, and melts at 202° with decomposition. It is different from the basic salt obtained by the addition of ferric acetate to ethylic ketophenylparaconate, being orange, not buff brown, and containing much less iron. In the decomposition of the red powder by cold water, some of the ethylic ketophenylparaconate was always produced, and could be isolated from the alcoholic mother liquor of the basic salt.

*Action of Ferric Chloride on the Lactone of Ethylic Oxalocitrate.*

Ethylic oxalocitrate was prepared from ethylic oxalacetoacetate by the action of aqueous potassium acetate, according to the directions given by Claisen and Hori (*Ber.*, 1891, 24, 120) ; it was purified by converting it into the barium salt, and decomposing the latter by dilute sulphuric acid.

Anhydrous ferric chloride, dissolved in ether (which had been dried over sodium), was freed from hydrochloric acid by shaking with iron filings, and added to the calculated quantity of the lactone of ethylic oxalocitrate. The ferric chloride used was always analysed, and the ratio of iron to chlorine agreed very nearly with that for  $\text{FeCl}_3$  ; the red oil which separated was washed thoroughly with ether, dried over sodium,

by pouring from one separating funnel to another. The last traces of ether were removed in a vacuum over sulphuric acid ; at the same time, acid fumes began to be evolved, although no ferrous iron could be detected. The oil became viscid, and a few crystals were visible. As we could not obtain the substance in crystals, the oil was analysed directly. The values for the iron were those for an additive product of ferric chloride and the lactone of ethylic oxalocitrate.

Fe = (1) 11·23; (2) 11·82; (3) 13·03; (4) 12·28 (12 days in a vacuum).

Cl = (1) 23·88; (2) 22·30; (3) 21·98; (4) 21·72 (14       ,,       ,,       ).

$\text{FeCl}_3 \cdot \text{C}_{14}\text{H}_{18}\text{O}_9$  requires Fe = 11·37 ; Cl = 21·62 per cent.

$\text{FeCl}_2 \cdot \text{C}_{14}\text{H}_{17}\text{O}_9$  requires Fe = 12·28 ; Cl = 15·57       ,,

It seemed as if the chemical behaviour of the compound would give more information regarding its composition than analyses of a substance which has, up to now, resisted all attempts to purify it completely.

The red oil is insoluble in benzene, carbon tetrachloride and light petroleum, sparingly soluble in ether, but readily so in alcohol and acetone.

The decomposition with water is similar to that in the case of the iron compound with ethylic ketophenylparaconate. Nine grams of the red oil, freed from ether in a vacuum, were washed rapidly with cold water, and then with warm water, until the washings were free from iron and chlorine; the oily residue became solid on being stirred with a glass rod. The solid can be dissolved in ether and precipitated as a red solid, by the addition of light petroleum, or it may be dissolved in methylic alcohol and precipitated by water. To obtain this solid pure, it may be redissolved in methylic alcohol and precipitated with water, or crystallised from benzene, in which it is easily soluble, separating out on evaporation in stout, rhombic prisms.

Analysis showed that this red substance was the iron salt of the lactone of ethylic oxalocitrate.

C = 48·35 ; H = 5·22 ; Fe = 5·30.

$\text{Fe}(\text{C}_{14}\text{H}_{17}\text{O}_9)_3$  requires C = 48·32 ; H = 4·89 ; Fe = 5·37 per cent.

The iron salt melts at 163° with decomposition. In order to investigate the decomposition by water, the amounts of iron and chlorine washed out by water, and the weight of iron salt left, were estimated.

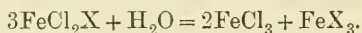
2·1243 grams of the oil, which had been standing several days in a vacuum over sulphuric acid, were washed, first with cold and then with hot water, about 500 c.c. of water being necessary to remove all the chlorine from the oil. The iron in the washings was estimated volumetrically by stannous chloride and potassium dichromate, the

chlorine by titration with excess of silver nitrate and ammonium thiocyanate.

Fe = 10.52; Cl = 22.56 per cent.

The oil which was treated with water was part of the sample containing 13.03 per cent. of Fe and 23.88 per cent. of Cl, but had stood for a longer time in a vacuum over sulphuric acid.

The weight of the iron salt left was 0.7013 gram. If the substance were an additive product, then water would decompose it, and at the same time some free hydrochloric acid, produced by the action of excess of water on the ferric chloride, would act on the iron salt, with the production of the soluble basic ferric chloride and the lactone ethereal salt. If, on the other hand, the compound  $\text{FeCl}_2\text{X}$  existed, then it would undergo decomposition according to the equation



That the iron salt itself exists in the oil is unlikely, for benzene does not take up the oil, whilst the iron salt is very easily soluble in that solvent.

In the case of the sodium salt of the lactone of ethylic oxalocitrate dissolved in dry benzene, a red solution was produced, without any separation of oil, when dry ethereal ferric chloride was added in the proportions to give  $\text{FeCl}_2\text{X}$  or  $\text{FeX}_3$ . This points to the formation of an iron salt of the type  $\text{FeX}_3$ , since the latter substance is soluble in benzene, whereas the additive product, or the  $\text{FeCl}_2\text{X}$  compound, is insoluble.

Further attempts are being made to obtain other similar red and violet ferric chloride compounds in a purer form.

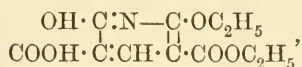
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#### XXXIV.—*Formation of aa'-Dihydroxypyridine.*

By SIEGFRIED RUHEMANN, Ph.D., M.A.

SOME years ago (Trans., 1893, 63, 259, 874), I showed that similar to the transformation of ethylic aconitate into citrazinamide is the condensation of alkyl derivatives of ethylic glutaconate with ammonia, and that this reaction leads to the formation of homologues of *aa'*-dihydroxypyridine. The dihydroxypyridine itself, however, which is undoubtedly formed in the interaction of ethylic glutaconate and ammonia, could not be isolated on account of the rapidity with which it is oxidised by the oxygen of the air (Trans., 1891, 59, 743). The same difficulty

was experienced by Guthzeit and Dressel (*Ann.*, 1891, 262, 113); in studying the action of heat on monethylic ethoxy- $\alpha$ -pyridonedicarboxylate,



they found that the latter was partially transformed into the diethylic salt of the dicarboxylic acid, together with a substance which, from its behaviour, they concluded to be  $\alpha$ -ethoxy- $\alpha'$ -hydroxypyridine, but were unable to isolate it owing to the ease with which it is attacked by atmospheric oxygen.

According to a statement by Anschütz (compare V. v. Richter's *Chemie der Kohlenstoffverbindungen*, 1896, pp. 519 and 527), Kekulé obtained dihydroxypyridine by the action of concentrated sulphuric acid on the diamide of  $\beta$ -hydroxyglutaric acid, on glutaminic acid, and also on the diamide of glutaconic acid, but an account of Kekulé's experiments did not appear in any chemical journal.

I found that *aa'*-dihydroxypyridine can readily be obtained from *aa'*-dihydroxydinicotinate. In a paper which I recently published in conjunction with K. C. Browning (*Trans.*, 1898, 73, 280), it has been shown that this ethereal salt is formed in the action of hydrochloric acid on ethylic dicyanoglutaconate, and that, on prolonged boiling with the acid, a decomposition takes place with formation of a substance which was regarded as *aa'*-dihydroxypyridine. A closer examination has confirmed this assumption.

On boiling the solution of ethylic dihydroxydinicotinate in concentrated hydrochloric acid for 2 hours in a reflux apparatus, the hydrolysis, accompanied by the removal of carbon dioxide, is completed. The solution, when concentrated under diminished pressure on the water bath, deposits almost colourless needles on cooling; these are washed with concentrated hydrochloric acid, in which they are sparingly soluble, and dried in a vacuum over potash and sulphuric acid. The substance was found to be the hydrochloride of *aa'*-dihydroxypyridine.

0.2515 gave 20.5 c.c. nitrogen at 16° and 762 mm. N = 9.52.

0.2325 „ 0.2372 AgCl. Cl = 24.13.

C<sub>5</sub>NH<sub>3</sub>(OH)<sub>2</sub>.HCl requires N = 9.49; Cl = 24.06 per cent.

The hydrochloride is rather unstable; on heating at 100°, it gradually loses hydrogen chloride, and the dissociation into the acid and dihydroxypyridine is also partially brought about by the action of water.

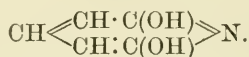
The solution of the salt in dilute hydrochloric acid reduces silver and platinum salts, and in contact with the skin develops purple spots after some time; a few drops of ferric chloride produce a red-violet



coloration, which, however, disappears on the addition of an excess of the metallic chloride, a black, flocculent precipitate being thrown down.

On carefully adding ammonia to the solution of the hydrochloride, the dihydroxypyridine is precipitated in slightly coloured prisms which dissolve in water as well as in alcohol, on boiling, and melt at 192—193° (the melting point of the compound prepared by Kekulé is given by Anschütz, *loc. cit.*, as 182—183°). When dry, it is moderately stable; on exposure to moist air, however, it is oxidised, becoming green.

The following analytical data correspond with the formula



0.2030 gave 0.4025 CO<sub>2</sub> and 0.0860 H<sub>2</sub>O. C = 54.07; H = 4.70.

0.2324 „ 25.5 c.c. nitrogen at 180° and 757 mm. N = 12.64.

C<sub>5</sub>H<sub>5</sub>NO<sub>2</sub> requires C = 54.05; H = 4.50; N = 12.61 per cent.

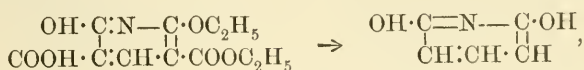
In a former note on the homologues of *aa'*-dihydroxypyridine (*Ber.*, 1893, 26, 1559), I pointed out the chemical analogy between them and resorcinol. This similarity is also exhibited by dihydroxypyridine itself. As the former is readily oxidised in the presence of ammonia with formation of a blue dye, so does an ammoniacal solution of dihydroxypyridine become indigo-blue when exposed to the atmosphere.

*Formation of aa'-Dihydroxypyridine from Monethylic  
Ethoxy-α-pyridonedicarboxylate.*

The transformation of ethylic dihydroxydinicotinate into *aa'*-dihydroxypyridine leads to the view that the product of the action of ammonia on ethylic ethoxypyronedicarboxylate (Guthzeit and Dressel, *loc. cit.*), namely, monethylic ethoxy-α-pyridonedicarboxylate, under the influence of hydrochloric acid, would be converted into *aa'*-dihydroxypyridine. Guthzeit and Dressel have already subjected ethoxyhydroxydinicotinic acid, formed from the above ethereal salt by boiling it with alkali, to the action of hydrochloric acid, with the view of obtaining dihydroxypyridine. They found, however, that fuming hydrochloric acid, acting at 130—140°, decomposes the pyridine derivative into ammonium chloride and glutaconic acid. Such a destruction of the pyridine-ring, I observed, does not take place if monethylic ethoxy-α-pyridonedicarboxylate is boiled with concentrated hydrochloric acid in a reflux apparatus. The pyridine compound, which differs from ethylic dihydroxydinicotinate, inasmuch as it does not dissolve in the acid at the ordinary temperature, on boiling enters into solution with evolution of carbon dioxide; the boiling is continued for 2—3 hours,

and the *aa'*-dihydroxypyridine thus formed is isolated in the manner previously stated.

The following symbols suffice to indicate the mode of its formation.



The identity with the substance obtained from ethylic dihydroxydinicotinate was verified by its behaviour, and by a nitrogen determination.

0.2638 gave 21.8 c.c. nitrogen at 18° and 758 mm.  $N = 9.47$ .

$\text{C}_5\text{NH}_3(\text{OH})_2\text{HCl}$  requires  $N = 9.49$  per cent.

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### XXXV.—*The Preparation and Properties of Formaldoxime.*

BY WYNDHAM R. DUNSTAN, M.A., F.R.S., and ARNOLD L. BOSSI, Ph.D.

IN a previous communication (Proc., 1894, p. 55), the authors have given a preliminary account of the isolation and chief properties of the oxime of formaldehyde, a compound to which particular interest attaches owing to its being the first member of the acetic series of aldoximes. The only previously recorded work on this subject is that of Scholl (*Ber.*, 24, 573), who, by the interaction of formaldehyde and hydroxylamine, obtained a white, amorphous solid which behaved as a polymeride of the oxime. By heating this solid polymeride, Scholl obtained the aldoxime itself as a vapour (of which the density was determined) and also in solution, but it could not be isolated for purposes of examination as liquid or solid, owing to the readiness with which it reverted into the solid polymeride. From the properties of the solutions formed on heating the polymeride with certain liquids, Scholl showed that formaldoxime is a powerful reducing agent, that it undergoes hydrolysis into formaldehyde and hydroxylamine, and that its vapour density corresponds with the formula  $\text{CH}_2\text{:NOH}$ .

The authors have succeeded in isolating formaldoxime as a liquid boiling at 83–85°. This liquid very rapidly changes into the solid amorphous polymeride, and could not be crystallised. A determination of the molecular weight of the liquid showed that it corresponds with the formula  $\text{CH}_2\text{:NOH}$ . The liquid burns with a livid flame, producing considerable quantities of hydrogen cyanide ( $\text{CH}_2\text{:NOH} = \text{H}_2\text{O} + \text{HCN}$ ). In the absence of water, the oxime combines with acids to form salts, several of which have been crystallised;

the hydrobromide and the hydrochloride in particular are well-defined, crystalline compounds, which are readily prepared in the pure state. Their analysis has disclosed the remarkable and unexpected fact that they contain three proportions of formaldoxime combined with one proportion of acid,  $(\text{CH}_2\text{:NOH})_3\text{HCl}$  and  $(\text{CH}_2\text{:NOH})_3\text{HBr}$ .

By the action of alkali metals on a dry ethereal solution of formaldoxime, metallic derivatives are obtained; the sodium derivative  $(\text{CH}_2\text{:NONa})$ , which is crystalline, very readily loses water forming sodium cyanide, and explodes when heated. Formaldoxime acts as a powerful reducing agent on solutions of many metallic salts, silver, gold, and mercury being precipitated as metals, whilst cupric salts are reduced to cuprous compounds; in the case of cupric sulphate, the oxime apparently combines in the first instance with the salt to form a crystalline compound.

The mode in which formaldoxime undergoes hydrolysis is of considerable theoretical interest. When heated with dilute acids, it is partly converted into formaldehyde and hydroxylamine and partly into formic acid and ammonia, the extent to which each of the changes takes place depending on the amount of water as well as on the temperature and time during which the liquid is heated. It is clear from this that either the oxime is susceptible of the remarkable isomeric change first observed to occur with certain oximes by Beckmann, or perhaps more probably that it is capable of existing in the tautomeric form. As a result, the formaldoxime undergoes partial conversion into its isomeride, formamide,  $\text{H}\cdot\text{CO}\cdot\text{NH}_2$ , which hydrolyses into formic acid and ammonia. When, however, formaldoxime is hydrolysed by contact with strong hydrochloric acid, it is quantitatively converted, without isomeric change, into hydroxylamine and formaldehyde.

Formaldoxime may be converted into crystalline acetyl and benzoyl derivatives. The acetyl formaldoxime is a well-defined compound, having a molecular weight corresponding with the formula  $(\text{CH}_2\text{:NO}\cdot\text{CH}_3\text{CO})_3$ , and the benzoyl derivative is a stable compound melting sharply at  $168.5^\circ$ .

When the oxime or its hydrochloride is reduced in either alkaline or acid solution, the nitrogen appears entirely as ammonia, but when the acetyl derivative is reduced, 2 atoms of the nitrogen appear as ammonia, and the third as methylamine. This result is somewhat difficult to interpret. It may be supposed that, under the conditions of the experiment, the acetyl formaldoxime is partly changed into the isomeric acetylformamide. Methyl iodide readily combines with formaldoxime, furnishing a crystalline compound,  $(\text{CH}_2\text{:NOH})_3\text{CH}_3\text{I}$ , of which an account has been already given (Dunstan and Goulding, *Trans.*, 1897, 71, 575). Here, again, the nitrogen of 1 molecule of the oxime behaves in a different manner from that of the other two.

*Preparation of Formaldoxime.*

When an aqueous solution of formaldehyde is mixed with a solution of hydroxylamine hydrochloride to which sufficient soda or sodium carbonate has been added to liberate the hydroxylamine, much heat is evolved, and if the liquid is allowed to stand at the ordinary temperature the solid polymeride of formaldoxime separates as a white, gelatinous precipitate. If, however, the liquid while still warm is shaken several times with ether almost immediately after the two solutions have been mixed, the oxime is obtained as an ethereal solution which does not readily polymerise unless it is highly concentrated. When this ethereal solution is well dried with potassium carbonate or calcium chloride, and the ether distilled off at the lowest possible temperature, a colourless liquid remains which rapidly polymerises to a white jelly as the temperature falls. With care, however, it may be fractionally distilled, especially if the distillates are kept slightly warm, and by this means a colourless mobile liquid may be obtained which distils constantly at 83—85°. It is, however, impossible to prevent the loss of some of the liquid, owing to the formation of the polymeride, and in any case the pure substance gradually gelatinises as it cools to the ordinary temperature. This method is, moreover, difficult to carry out unless pure materials are employed. The presence of methylic alcohol or acetone in the solution of formaldehyde used very much complicates the process of purification, in fact, it is exceedingly difficult to separate from the compound any acetoxime it may contain. Inasmuch as nearly all commercial ether contains acetone, the ether used in the experiments must be specially purified (by alkali hydrogen sulphite) from this substance.

A much more satisfactory method of obtaining the pure liquid oxime consists in decomposing with alkalis the crystalline hydrochloride which is readily prepared by passing gaseous hydrogen chloride into the well-dried ethereal solution of the oxime (see below). When this salt is dissolved in water, it dissociates into the oxime and hydrochloric acid, and if this acid solution is at once exactly neutralised and distilled, the pure oxime is obtained after several fractionations. The best yield is obtained by placing about 25 grams of the pure and dry hydrochloride in a dry distillation flask, and then adding the quantity of powdered potash requisite to react with the hydrogen chloride. The mixture is well cooled with ice, and then small pieces of ice are introduced into the flask, which is allowed gradually to attain the temperature of the air. The liquid is distilled under reduced pressure (40—50 mm.), the receiver being kept at 40—50° to prevent polymerisation. The large fraction which comes over first is distilled under the



ordinary pressure, when nearly the whole of it is obtained between 83° and 85°.

Formaldoxime is a colourless, highly refractive liquid boiling at 84°. It burns with a livid green flame which generates much hydrogen cyanide,  $\text{CH}_2\text{:NOH} = \text{H}_2\text{O} + \text{HCN}$ . At the ordinary temperature, it gradually gelatinises, and is largely converted into the white, amorphous polymeride; this change takes place less readily at higher temperatures. We have made numerous observations on the conditions under which this change takes place, but they have led to nothing beyond the fact that heat retards the change, that light has no influence in promoting it, and that the addition of minute quantities of various substances appeared to have little or no effect in delaying or accelerating the polymerisation. The extent of the change seems to be a function of the temperature, and the change is reversible. When heated in a closed two-limbed tube, the dry polymeride is converted at about 140° into the liquid oxime, which distils into the other limb; as Scholl has shown, the solid polymeride may also be reconverted into a solution of the oxime by heating it with water or other neutral liquids, the insoluble polymeride gradually passing into solution as the liquid oxime.

We have succeeded in determining the molecular weight of the liquid oxime by Raoult's method, using acetic acid as the solvent. In this, warmed to 60°, the liquid oxime was distilled.

	I.	II.
Weight of oxime .....	0.4014	0.39662
Weight of solvent.....	30.9693	39.1127
Depression .....	1.22°	0.92°
M. W. ....	41.6	M. W. = 43

The molecular weight calculated from the formula  $\text{CH}_2\text{:NOH}$  is 45. This result agrees with Scholl's determination of the molecular weight by taking the density of the vapour evolved on heating the solid polymeride.

All attempts to crystallise formaldoxime have failed; when cooled, it changes into the polymeride, and could not be "touched off" by the addition of other crystalline oximes of the same series.

*Formaldoxime Hydrochloride*,  $(\text{CH}_2\text{:NOH})_3\text{HCl}$ . — When gaseous hydrogen chloride is passed into a dry ethereal solution of formaldoxime, a white precipitate is thrown down. This precipitate does not appear to be crystalline, but on dissolving it in pure methylic alcohol and gradually adding ether, it is obtained in well-defined, prismatic crystals which melt at 136°; the same substance may be prepared by passing hydrogen chloride into a solution of the oxime in methylic alcohol, or by acting with gaseous hydrogen chloride on the white, solid poly-



meride. It exhibits all the properties of a true hydrochloride of the oxime. The addition of alkali, or even of water, sets free the oxime, and on hydrolysis with dilute acid the salt furnishes formaldehyde and hydroxylamine.

Determinations of chlorine in the recrystallised compound led to the following results.

0.1525 gave 0.1330 AgCl. Cl = 21.37 per cent.

0.2380 „ 0.1910 AgCl. Cl = 19.91 „

$(\text{CH}_3\text{NO})_3\text{HCl}$  requires Cl = 20.7 per cent.

Determinations of chlorine in a number of different specimens several times recrystallised gave results confirming those recorded above.

The remarkable fact is therefore established that three molecules of the oxime combine with one of hydrogen chloride.

As already stated, the production of this hydrochloride is the best means of obtaining the oxime in a pure state.

*Formaldoxime Hydrobromide*,  $(\text{CH}_3\text{NO})_3\text{HBr}$ .—When gaseous hydrogen bromide is passed into an ethereal solution of the oxime, a white precipitate is thrown down, which can be obtained in prismatic crystals on adding ether to its solution in methylic alcohol. In appearance, the salt closely resembles the hydrochloride, and, like it, dissociates when mixed with water, hydrobromic acid being liberated.

Analyses of three recrystallised specimens of the salt furnished the following percentages of bromine: (I) 36.6, (II) 36.9, (III) 37.5. Calculated for  $(\text{CH}_3\text{NO})_3\text{HBr}$ , 36.9.

*Formaldoxime Hydriodide*.—This salt is formed by passing gaseous hydrogen iodide into a well-dried ethereal solution of formaldoxime. By adding ether to its solution in methylic alcohol, it is obtained in prismatic crystals which melt at  $136^\circ$ , at which temperature the salt is completely decomposed.

*Acetylformaldoxime*,  $(\text{CH}_2\text{:NO}\cdot\text{CO}\cdot\text{CH}_3)_3$ .—When the requisite quantity of acetic anhydride is gradually added to a dry ethereal solution of the oxime and the mixture is allowed to stand, large, well-defined crystals separate which are very stable. The compound dissolves readily in water, and the aqueous solution may be boiled without any appreciable decomposition taking place; as the solution cools, the compound crystallises out unchanged. In this manner, it may be recrystallised. It melts at  $133^\circ$ , with partial decomposition.

Analyses by combustion gave the following results.

(I) C = 41.18; H = 6.07 per cent. (II) C = 41.10; H = 6.05 per cent. (III) N = 16.04 per cent.

$\text{CH}_2\text{:NO}\cdot\text{CO}\cdot\text{CH}_3$  requires C = 41.37; H = 5.75; N = 16.09 per cent.

The molecular weight was determined by Raoult's method, using acetic acid as the solvent.

Weight of acetyl derivative, 0.0467 gram; weight of solvent, 3.3240 grams.

Depression of freezing point,  $0.21^{\circ}$ ; whence  $M. W. = 266.5$ .

Calculated for  $(CH_2:NO \cdot CO \cdot CH_3)_3 - 261$ .

It is remarkable that the oxime itself, under these conditions, should exhibit a molecular weight corresponding with the formula  $CH_2:NOH$ , whilst its acetyl derivative corresponds with the same triple molecular aggregate as is seen in the salts. That the compound is a true acetyl derivative is shown by the fact that, when boiled with dilute sulphuric acid, it furnishes acetic acid.

*Benzoylformaldoxime*,  $(CH_2:NO \cdot CO \cdot C_6H_5)_3$ .—If an ethereal solution of benzoic anhydride is mixed with an ethereal solution of the oxime, crystals separate on standing; these, after purification by recrystallisation from hot alcohol, are obtained in fine needles. The same substance may be procured by the action of benzoic chloride on the oxime in the presence of alkali or water alone. The crystals melt and decompose at  $159^{\circ}$ . The substance is remarkably stable; it is not decomposed by boiling with water, dilute acids, or alkalis, but strong aqueous alkalis or acids produce hydrolysis, with separation of benzoic acid. By decomposition with strong aqueous potash in a closed tube, 81.8 per cent. of benzoic acid was produced, which agrees well with the quantity calculated from the formula  $(CH_2:NO \cdot CO \cdot C_6H_5)_3$ , namely, 81.3 per cent.

#### *Hydrolysis of Formaldoxime.*

The mode of hydrolysis of formaldoxime being of considerable interest, it has been very carefully studied in the case of the oxime itself, the solid polymeride, the hydrochloride, and the acetyl derivative. The results of these experiments may be summarised as follows. When the oxime or its hydrochloride is heated with water under the ordinary conditions, or in a closed tube, very little hydrolysis occurs, and the change is not much greater if very dilute alkali is substituted for water.

When dilute hydrochloric acid or sulphuric acid is used as the hydrolysing agent, one portion of the oxime is resolved into formaldehyde and ammonia, and the other into formic acid and ammonia. The extent to which change occurs in one direction or the other (as measured by the quantity of hydroxylamine produced) depends chiefly on the dilution of the acid and on the temperature. When the hydrochloride was heated with ordinary hydrochloric acid in a closed tube at  $120^{\circ}$  for 2 hours, only 2.5 per cent. of hydroxylamine was found in the liquid, the calculated quantity being 42.5 per cent., assuming that the oxime undergoes hydrolysis in accordance with the equation  $CH_2:NOH + H_2O = H \cdot COH + NH_2 \cdot OH$ . In all the experiments in

which the oxime is hydrolysed by heating with dilute acid, relatively small quantities of hydroxylamine and large quantities of ammonia were obtained.

When the hydrochloride was heated with concentrated hydrochloric acid for from 6 to 7 minutes, 24 per cent. of hydroxylamine was produced, whilst the oxime or its hydrochloride, when left in contact with concentrated hydrochloric acid for 2 days in the cold, was entirely converted into formaldehyde and hydroxylamine without the production of any ammonia or formic acid. Similar results were obtained when the amorphous polymeride of the oxime was used. The acetyl derivative also behaved in the same manner. This derivative appears to be more readily decomposed than the oxime when heated in a closed tube with water, but in this case, as with dilute acid, very little hydroxylamine and much ammonia is produced; on the other hand, when the acetyl derivative is digested with cold concentrated hydrochloric acid, a large yield of hydroxylamine is obtained.

The production of ammonia and formic acid from formaldoxime instead of formaldehyde and hydroxylamine may be accounted for in several ways. It may be supposed that the oxime first undergoes dehydration into hydrogen cyanide, and that this then suffers hydrolysis into ammonia and formic acid. Stereochemical considerations would favour this view of the change. We have, indeed, observed in several of these experiments that some hydrogen cyanide is formed. Another supposition is, that the oxime undergoes isomeric change into its

isomeride, formamide, 
$$\begin{array}{c} \text{H} \cdot \text{C} \cdot \text{H} \\ | \\ \text{N} \cdot \text{OH} \end{array} \rightarrow \begin{array}{c} \text{H} \cdot \text{C} \cdot \text{O} \\ | \\ \text{NH}_2 \end{array},$$
 under the conditions of

the experiment. As, however, stereochemically there is no particular reason why this change should occur in the case of formaldoxime, it seems

more probable that a tautomeric form,  $\begin{array}{c} \text{H} \cdot \text{C} \cdot \text{OH} \\ | \\ \text{NH} \end{array}$  or  $\begin{array}{c} \text{H}_2\text{C} \\ | \\ \text{HN} \end{array} > \text{O}$ , of the

oxime is primarily responsible for the production of formic acid and ammonia.

### *Reduction of Formaldoxime.*

In connection with the question of the constitution of formaldoxime, and especially of the existence of a tautomeric form, it was important to ascertain the fate of the nitrogen on reduction. When the hydrochloride of the oxime is reduced in the ordinary manner with stannous chloride, the whole of the nitrogen appears as ammonia, and the same result is obtained when other reducing agents are employed.

When, however, the acetyl derivative is reduced, the nitrogen appears partly as ammonia and partly as methylamine; by careful reduction with acetic acid and zinc dust, it was established that one-third of the nitrogen is reduced to ammonia and two-thirds to methyl-

amine, and the same result was obtained on effecting the reduction with sodium amalgam and dilute sulphuric acid. The methylamine hydrochloride was identified after separation from the ammonium chloride by means of a mixture of alcohol and ether, whilst the proportion of the two salts present was ascertained by converting the mixture into platinichloride, in which the platinum was determined.

It thus appears that, of the three residues of oxime present in the acetyl derivative,  $(\text{CH}_2\cdot\text{NO}\cdot\text{CO}\cdot\text{CH}_3)_3$ , one is reduced to ammonia and two to methylamine. This result may be explained by the supposition that two molecules of the substance suffer decomposition into acetic acid and hydrogen cyanide, and that the hydrogen cyanide is then reduced to methylamine. The fact that a constant proportion of methylamine is obtained, points to the conclusion that, in the complex  $(\text{CH}_2\cdot\text{NO}\cdot\text{CO}\cdot\text{CH}_3)_3$ , two atoms of nitrogen are united differently from the third, but we have no sufficient evidence to warrant any supposition as to the structure of this molecular aggregate. The same peculiarity has been observed in the compound of formaldoxime with methylic iodide (Dunstan and Goulding, *loc. cit.*).

#### *Action of Alkyl Iodides on Formaldoxime.*

Alkyl iodides appear to combine readily with formaldoxime; the compound formed by its union with methylic iodide,  $(\text{CH}_3\text{NO})_3\text{CH}_3\text{I}$ , which is a well crystallised compound, has been already fully examined and described (Dunstan and Goulding, *loc. cit.*). On hydrolysis, only one atom of nitrogen appears as methylamine.

#### *Other Reactions of Formaldoxime.*

*Action of Bromine.*—Bromine acts readily on an ethereal solution of the oxime; the chief products are the hydrobromide of the oxime, an oily liquid ( $\text{CHBr}\cdot\text{NOH}$ ), which has proved to be so difficult to separate in a pure state that its composition has not so far been established with certainty, and an unstable, crystalline substance decomposing with violence when warmed, even in solution, to  $40\text{--}50^\circ$ , leaving a residue consisting chiefly of hydroxylamine hydrobromide. This compound has not been completely identified, but its formula appears to be  $\text{CNOH}\cdot\text{HBr}$ , and its properties correspond closely with those of the compound of the formula  $\text{CNOH}\cdot\text{HCl}$ , which has been described by Scholl and by Nef as resulting from the action of hydrochloric acid on fulminates.

*Action of Phosphoric Anhydride.*—Phosphoric anhydride does not act in the cold, but, on warming, a violent action takes place, and hydrogen cyanide is abundantly produced.

*Action of Alkali Metals.*—Potassium and sodium act on an ethereal



solution of formaldoxime, evolving hydrogen and forming metallic derivatives of the oxime. The sodium derivative,  $\text{CH}_2\text{:NONa}$ , is crystalline; when gently warmed, it explodes, leaving a residue principally consisting of sodium cyanide.

*Action of Metallic Salts.*—Formaldoxime acts as a powerful reducing agent on many metallic salts; when warmed with aqueous solutions of mercuric chloride, silver nitrate, auric chloride, and copper sulphate, the corresponding metals are precipitated.

If formaldoxime dissolved in methylic alcohol or water is added to a cold saturated solution of cupric sulphate, the liquid becomes dark green and acid in reaction from the presence of free sulphuric acid, and soon deposits deep green, prismatic crystals; these are very sparingly soluble in cold water, and are gradually decomposed by hot water. When kept, they slowly undergo a remarkable decomposition, the principal products of which are nitric oxide, hydrogen cyanide, and apparently sulphur dioxide.

Although a number of analyses of different specimens of the salt have been made, closely concordant results have not been obtained; this remarkable compound needs further investigation before a definite formula can be assigned to it. By titrating the acid liberated on mixing an excess of the oxime with a solution of cupric sulphate of known strength, it was ascertained that one molecular proportion of sulphuric acid is liberated for every three molecules of copper sulphate present. After the copper compound has been boiled with sulphuric acid (40 per cent.), no hydroxylamine can be detected in the residue, but only ammonium sulphate and cupric sulphate.

The effect of formaldoxime on other metallic salts is also remarkable. *Ferric chloride* in dilute neutral solution becomes a deep plum colour. *Nickel sulphate* in dilute solution becomes dark green. *Manganese sulphate* in aqueous solution becomes dark red. *Potassium sulphate* in cold saturated solution apparently forms a well-crystallised compound.

In conclusion, we wish to record our thanks to Mr. Ernest Goulding for the assistance he has given us in connection with this inquiry.

### XXXVI.—*Action of Ammonia and Substituted Ammonias on Acetylurethane.*

By GEORGE YOUNG, Ph.D., and ERNEST CLARK.

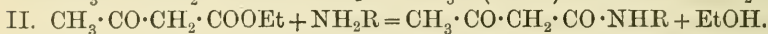
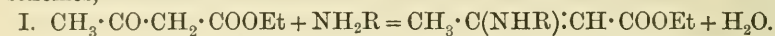
ON comparing the constitutional formula of ethylic acetoacetate  $\text{CH}_3\cdot\text{CO}\cdot\text{CH}_2\cdot\text{COOC}_2\text{H}_5$ , with that of acetylurethane,



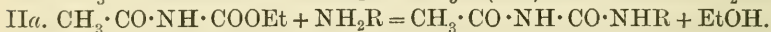
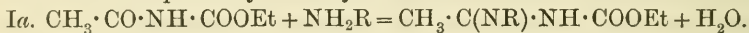
a striking analogy is evident, but hitherto little work has been done



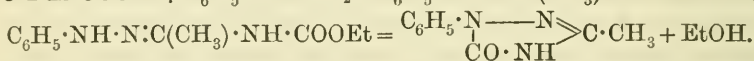
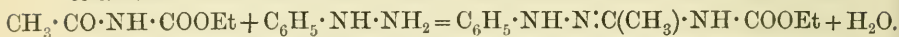
towards instituting a comparison of the reactions of the two compounds. The present research was undertaken with a view of studying the action of ammonia and of substituted ammonias on acetylurethane as compared with the corresponding actions on ethylic acetoacetate. The latter forms two series of derivatives, as represented by the two schemes,



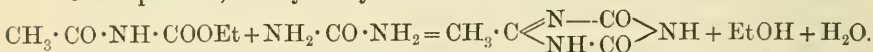
and acetylurethane, if it acted analogously, would form derivatives of acetamidine respectively of acetylcarbamide.



Andreocci (*Gazzetta*, 1889, 19, 448) found that phenylhydrazine and acetylurethane yielded phenylmethyloxytriazole in the same way that phenylmethylpyrazolone is formed by the interaction of phenylhydrazine and ethylic acetoacetate. The formation of phenylmethyloxytriazole took place in two stages; the first, similar to Ia, the second to IIa.



It has also been observed by Ostrogovitch (*Annalen*, 1895, 288, 318; 1896, 291, 377) that carbamide and acetylurethane interact according to both of the above schemes Ia and IIa, yielding a closed chain product, methyldioxytriazine.



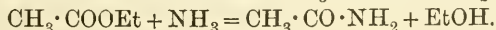
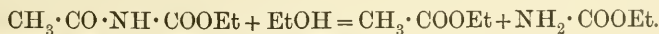
We have confined our investigations to substituted ammonias unlikely to give rise to cyclo-compounds, and, as is shown by the experimental results described in the following pages, the action of ammonia or of a substituted ammonia on acetylurethane leads, under most conditions, to the formation of an acetylcarbamide. In no case have we been able to isolate an amidine, but, under certain conditions, we have obtained acetamide and acetylpyrrolidine, in considerable amounts, by the action of ammonia and of pyrrolidine, as also smaller quantities of acetanilide, acetylnaphthylamine, and acetylphenylcarbamide by the action of aniline, naphthylamine, and phenylcarbamide. These products may be ascribed to hydrolysis of acetamidine derivatives formed according to scheme Ia. This point is discussed in the description of the action of alcoholic ammonia. The general results of the investigation point, further, to a close relation between the basicity of an ammonia and its capability of acting on acetylurethane. Ammonia and methylamine act easily at the ordinary temperature; aniline, naphthylamine and carbamide, ammonias of weaker basicity but still

capable of forming stable salts, require somewhat higher temperatures ranging from 120° to 140°. Substituted ammonias, such as diphenylamine, acetanilide, and acetylcarbamide, which do not form stable hydrochlorides, appear to be without action.

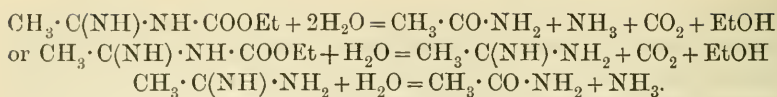
*Action of Ammonia.*—Kretzschmar (*Ber.*, 1875, 8, 103) states that the action of alcoholic ammonia on acetylurethane is similar to that of alcoholic potash as represented by the equation  $\text{CH}_3 \cdot \text{CO} \cdot \text{NH} \cdot \text{COOEt} + 2\text{KHO} = \text{K}_2\text{CO}_3 + \text{NH}_3 + \text{CH}_3 \cdot \text{COOEt}$ . Although not definitely stated, it is to be inferred that the action of alcoholic ammonia would yield ethylic acetate and ammonium carbonate,  $\text{CH}_3 \cdot \text{CO} \cdot \text{NH} \cdot \text{COOEt} + \text{NH}_4 \cdot \text{OH} + \text{H}_2\text{O} = (\text{NH}_4)_2\text{CO}_3 + \text{CH}_3 \cdot \text{COOEt}$ .

Our studies on the action of ammonia on acetylurethane, both in alcoholic and aqueous solutions, and under varying conditions as to temperature and pressure, have shown that the action indicated by Kretzschmar takes place only to a small extent. When acetylurethane was left in contact with alcoholic ammonia at the ordinary temperature, ethylic acetate and acetylcarbamide were formed. Both actions took place very slowly, as, even after some days, much acetylurethane remained unchanged. On repeating this experiment at the boiling point of water, neither ethylic acetate nor acetylcarbamide could be found in the product, but acetamide had been formed to the extent of 97 per cent. of that required by the equation,  $\text{CH}_3 \cdot \text{CO} \cdot \text{NH} \cdot \text{COOEt} + \text{H}_2\text{O} = \text{CH}_3 \cdot \text{CO} \cdot \text{NH}_2 + \text{EtOH} + \text{CO}_2$ . At 150°, under pressure, the action reverted to the formation of acetylcarbamide, and that to such an extent that the product contained little more than traces of acetamide.

The formation of acetamide as shown by the above equation would be analogous to the ketone hydrolysis of ethylic acetoacetate; this explanation is unsatisfactory because if, in the place of alcoholic ammonia, an alcoholic solution of a substituted ammonia be used (see action of aniline, &c.), an acetylamine is formed, showing that the nitrogen of the acetamide is derived, not from the urethane, but from the ammonia. This fact might be accounted for in two ways. Firstly, by supposing the action to take place in the two following stages.



Against this view may be set the fact that acetylurethane remains unchanged when heated with alcohol in a reflux apparatus on the water bath. The second and, we think, more probable explanation of the formation of acetamide is that the action of ammonia on acetylurethane takes place primarily according to scheme Ia, with formation of acetamidineurethane, which is then hydrolysed, either directly or with intermediate formation of acetamidine, to acetamide.



In the foregoing experiments, no trace of acetamidine could be discovered amongst the products, a result which was to be expected in view of the well-known instability of this substance. Since acetamidine is much more stable in the form of its hydrochloride, and as this salt is formed by the action of ammonium chloride, we endeavoured to prevent the last stage of the hydrolysis taking place, by adding ammonium chloride to the mixture. In this case also no trace of acetamidine could be detected.

Whilst, as just described, the action of alcoholic ammonia on acetylurethane yields various products under varying conditions, the action of aqueous ammonia is more simple; whether at the ordinary temperature, at that of the water bath in a reflux apparatus, or at higher temperatures under pressure, acetylcarbamide alone is found, no trace of either ethylic acetate or acetamide could be detected. At 150° under pressure, the acetylcarbamide was hydrolysed, carbamide being obtained. The effect of passing dry gaseous ammonia into an ethereal solution of acetylurethane was also tried, but on evaporating the ether, the acetylurethane remained unchanged.

The acetamide obtained in these reactions was recognised by its odour, its melting point (82—83°), and its boiling point (223° at 751 mm.). The specimens of acetylcarbamide obtained by the foregoing reactions each melted, after recrystallisation, at 218—219°. (Behrend gives 212°; *Annalen*, 1885, 229, 30). A comparison was therefore made with acetylcarbamide prepared by the action of acetyl chloride on carbamide; the product, after recrystallisation from 50 per cent. alcohol, melted at 218—219°. The acetylcarbamide from acetylurethane was analysed.

0.1248 gave 0.1610 CO<sub>2</sub> and 0.0664 H<sub>2</sub>O. C = 35.18; H = 5.91.

CH<sub>3</sub> · CO · NH · CO · NH<sub>2</sub> requires C = 35.29; H = 5.88 per cent.

*Action of Methylamine.*—On allowing methylamine either in aqueous or alcoholic solution to act on acetylurethane at the ordinary temperature and evaporating the solution in a vacuum, prisms of acetylmethylcarbamide melting at 179—180° were obtained. At higher temperatures under pressure, the result was the same, but at 150°, using an aqueous solution, a small amount of methylcarbamide was also obtained. Neither acetamide nor methylacetamide could be found amongst the products of the action, which had, therefore, taken place entirely according to scheme II*a*. The acetylmethylcarbamide obtained from acetylurethane was analysed.

0.1920 gave 0.2920  $\text{CO}_2$  and 0.1176  $\text{H}_2\text{O}$ .  $\text{C} = 41.47$ ;  $\text{H} = 6.80$ .

$\text{CH}_3 \cdot \text{CO} \cdot \text{NH} \cdot \text{CO} \cdot \text{NH} \cdot \text{CH}_3$  requires  $\text{C} = 41.37$ ;  $\text{H} = 6.89$  per cent.

The amount of methylcarbamide obtained was too small to allow of analysis; it was recognised by its melting point ( $102^\circ$ ), and by the melting point of its nitrate ( $128^\circ$ ).

*Action of Aniline.*—Aniline did not act on acetylurethane at  $100^\circ$  even on prolonged heating, but under pressure, and at temperatures ranging from  $125^\circ$  to  $160^\circ$  action took place, the product consisting principally of acetylphenylcarbamide, along with which there was always present a small amount of acetanilide. At  $125$ — $130^\circ$ , for 6 hours, the yield of acetylphenylcarbamide was over 60 per cent. of the theoretical. Changes in the strength of the alcohol used as solvent did not seem to effect the result. The acetylphenylcarbamide, after recrystallisation from hot water, melted at  $183^\circ$ .

0.1250 gave 0.2777  $\text{CO}_2$  and 0.0639  $\text{H}_2\text{O}$ .  $\text{C} = 60.59$ ;  $\text{H} = 5.68$ .

$\text{CH}_3 \cdot \text{CO} \cdot \text{NH} \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_6\text{H}_5$  requires  $\text{C} = 60.67$ ;  $\text{H} = 5.61$  per cent.

The acetanilide crystallised from water in characteristic leaves which melted at  $112$ — $114^\circ$ .

The action of aniline on acetylurethane took place, therefore, principally according to scheme IIa, and only to a small extent, if at all, according to Ia.

*Action of  $\alpha$ - and  $\beta$ -Naphthylamines.*—Preliminary experiments showed that little, if any, action takes place between  $\alpha$ -naphthylamine and acetylurethane at temperatures below  $130^\circ$ . Even at  $150^\circ$ , action takes place but slowly, as, after several hours heating, unchanged naphthylamine is still present. The product consists chiefly of acetyl- $\alpha$ -naphthylcarbamide, with small quantities of acetyl- $\alpha$ -naphthylamine, showing that, as in the case of aniline, action takes place according to both of the typical equations.

The acetyl- $\alpha$ -naphthylcarbamide formed white, microscopic needles which melted at  $214$ — $215^\circ$ , and was identical in its properties with the compound prepared by the action of acetic chloride on  $\alpha$ -naphthylcarbamide as described in a previous paper (Trans., 1897, 71, 1201).

0.1464 gave 0.3678  $\text{CO}_2$  and 0.0685  $\text{H}_2\text{O}$ .  $\text{C} = 68.51$ ;  $\text{H} = 5.19$ .

$\text{CH}_3 \cdot \text{CO} \cdot \text{NH} \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_{10}\text{H}_7$  requires  $\text{C} = 68.42$ .  $\text{H} = 5.26$  per cent.

For further identification, the acetyl derivative was hydrolysed by dilute caustic soda; the product crystallised from alcohol in delicate, white needles, which melted at  $213$ — $214^\circ$ , and in all respects agreed with that obtained by the action of potassium cyanate on  $\alpha$ -naphthylamine hydrochloride (*loc. cit.*). The  $\alpha$ -acetylnaphthylamine was recognised by its solubility in alcohol and its melting point ( $159$ — $160^\circ$ ).

The action of  $\beta$ -naphthylamine on acetylurethane took place in the



same manner and under the same conditions as that of  $\alpha$ -naphthylamine; the product consisted chiefly of  $\beta$ -acetylnaphthylcarbamide which formed delicate, white needles, melted at 202—203°, and agreed in its properties with the acetyl derivative prepared by the action of acetic chloride on  $\beta$ -naphthylcarbamide (Trans., 1897, 71, 1203).

0.1220 gave 0.3057  $\text{CO}_2$  and 0.0577  $\text{H}_2\text{O}$ .  $\text{C} = 68.33$ ;  $\text{H} = 5.25$ .  
 $\text{CH}_3 \cdot \text{CO} \cdot \text{NH} \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_{10}\text{H}_7$  requires  $\text{C} = 68.42$ ;  $\text{H} = 5.26$  per cent.

A small amount of  $\beta$ -acetylnaphthylamine was also isolated. It crystallised from hot water in long needles which melted at 130—132°.

*Action of Piperidine.*—By heating an alcoholic solution of piperidine and acetylurethane at 150—155°, a yellowish solution having a green fluorescence was obtained. From this, three products were isolated.

1. A solid—not hygroscopic—crystallising in flat, colourless plates which melted at 105—107°. This occurred in small amount.

2. An extremely hygroscopic solid crystallising in colourless needles which melted at 107.5—109°. This occurred in much larger quantities.

3. An oil boiling at about 220° under 760 mm. pressure. This was the principal product.

The solid, melting at 105—107°, was extremely soluble in water and alcohol, easily soluble in ether and hot benzene, less soluble in cold benzene and hot light petroleum; it agreed in its properties with piperidylcarbamide prepared by the action of potassium cyanate on piperidine hydrochloride.

0.1621 gave 0.3346  $\text{CO}_2$  and 0.1350  $\text{H}_2\text{O}$ .  $\text{C} = 56.29$ ;  $\text{H} = 9.25$ .

$\text{C}_5\text{H}_{10}\text{N} \cdot \text{CO} \cdot \text{NH}_2$  requires  $\text{C} = 56.25$ ;  $\text{H} = 9.37$  per cent.

This piperidylcarbamide is formed by the hydrolysis of the second product, which is apparently acetyl-piperidylcarbamide. Owing to its extremely hygroscopic nature, satisfactory analysis could not be obtained, but it agreed in its properties with the acetyl derivative formed by the action of acetic chloride on piperidylcarbamide. Acetyl-piperidylcarbamide crystallises from light petroleum in long, colourless needles which melt at 107.5—109°, and are extremely hygroscopic, very soluble in benzene, chloroform, and alcohol, less so in light petroleum. It is not extracted from its aqueous solution by ether.

The oil constituting the third product was fractionally distilled; the fraction passing over between 223° and 224°, at 750 mm., gave on analysis figures agreeing with those required for acetyl-piperidine, and on hydrolysis with strong hydrochloric acid it yielded piperidine.

0.1740 gave 0.4183  $\text{CO}_2$  and 0.1570  $\text{H}_2\text{O}$ .  $\text{C} = 65.56$ ;  $\text{H} = 10.02$ .

$\text{C}_5\text{H}_{10}\text{N} \cdot \text{CO} \cdot \text{CH}_3$  requires  $\text{C} = 66.14$ .  $\text{H} = 10.23$  per cent.

*Action of Phenylcarbamide.*—As has been shown by Ostrogovitch,

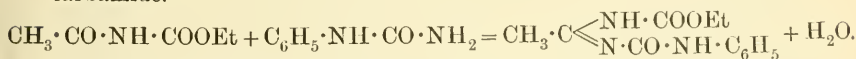


both the amidogen groups of carbamide react with acetylurethane, giving rise to a cyclo-compound.

Preliminary experiments with acetanilide showed that the group  $\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_5$  does not enter into action with acetylurethane. With phenylcarbamide, therefore, only one or other of the two possible actions would take place, the closing of the ring being prevented by the presence of the phenyl group. As product of the one action, acetylphenylbiuret,  $\text{CH}_3\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_5$ , was to be expected; of the other, analogously to the formation of acetamide, acetylphenylcarbamide.

Acetylurethane and phenylcarbamide were heated together, both with and without a solvent (alcohol, water), at temperatures ranging up to  $150^\circ$ . Below  $120^\circ$ , no action took place. Above that temperature, the product consisted chiefly of *s*-diphenylcarbamide and acetylphenylcarbamide, with small quantities of carbamide, cyanuric acid, and acetanilide; we could not discover any traces of acetylphenylbiuret or of phenylbiuret. Control experiments showed that phenylcarbamide, under similar conditions, yielded *s*-diphenylcarbamide, carbamide, cyanuric acid, and aniline. The small amount of aniline was just sufficient to account for the appearance of acetanilide amongst the products of the action with acetylurethane.

The action of acetylurethane and phenylcarbamide may be considered as resulting in the formation of an acetamidine which, under the conditions of the action, becomes hydrolysed to acetylphenylcarbamide.



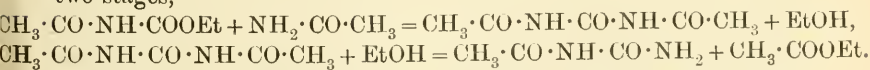
The *s*-diphenylcarbamide obtained melted at  $238\text{--}239^\circ$  and boiled at  $262^\circ$ .

0.1235 gave 0.3322  $\text{CO}_2$  and 0.0620  $\text{H}_2\text{O}$ .  $\text{C} = 73.38$ ;  $\text{H} = 5.58$ .

$\text{CO}(\text{NH}\cdot\text{C}_6\text{H}_5)_2$  requires  $\text{C} = 73.58$ ;  $\text{H} = 5.66$  per cent.

It is of some interest to note that phenylcarbamide yields considerable quantities of *s*-diphenylcarbamide when merely boiled with water.

*Action of Acetamide.*—When acetamide and acetylurethane are heated together at  $160^\circ$ , without a solvent, the product consists of acetylcarbamide and ethylic acetate. The action probably takes place in two stages,



The acetylcarbamide obtained melted, after recrystallisation from 50 per cent. alcohol, at  $218\text{--}219^\circ$ .

0.1537 gave 0.1983  $\text{CO}_2$  and 0.0818  $\text{H}_2\text{O}$ .  $\text{C} = 35.18$ ;  $\text{H} = 5.91$ .

$\text{CH}_3\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$  requires  $\text{C} = 35.29$ ;  $\text{H} = 5.88$  per cent.

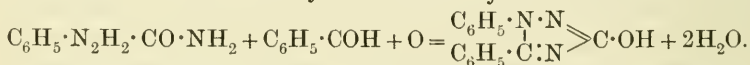
Diphenylamine, acetylcarbamide, and acetanilide were also heated with acetylurethane under varying conditions as to solvent, temperature, and pressure, but in no case could any product of interaction be observed.

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### XXXVII.—*Formation of Oxytriazoles from Semicarbazides.*

By GEORGE YOUNG, Ph.D., and BENJAMIN MITCHELL STOCKWELL, B.Sc.

IN previous papers (Trans., 1895, **67**, 1063; 1897, **71**, 200), it was shown that diphenyloxytriazole is formed when a mixture of phenylsemicarbazide and benzaldehyde is oxidised by alcoholic ferric chloride,



The action could also be carried out in the two separate stages,

1.  $\text{C}_6\text{H}_5\cdot\text{N}_2\text{H}_2\cdot\text{CO}\cdot\text{NH}_2 + \text{O} = \text{C}_6\text{H}_5\cdot\text{N}_2\cdot\text{CO}\cdot\text{NH}_2 + \text{H}_2\text{O}$
2.  $\text{C}_6\text{H}_5\cdot\text{N}_2\cdot\text{CO}\cdot\text{NH}_2 + \text{C}_6\text{H}_5\cdot\text{COH} = (\text{C}_6\text{H}_5)_2\text{C}_2\text{N}_3\cdot\text{OH} + \text{H}_2\text{O}.$

In place of benzaldehyde, other aromatic aldehydes, such as nitrobenzoic, toluic, terephthalic, and cinnamic aldehydes could be used, but not fatty aldehydes, such as formic, acetic, and isobutyric aldehydes. The action has now been applied to other semicarbazides of the type  $\text{R}\cdot\text{NH}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$ , and so far as the investigation has extended the results show the above method of forming oxytriazoles to be applicable to all semicarbazides of this type, whether R be a fatty or an aromatic radicle.

The present paper contains an account of some oxytriazoles formed from aromatic semicarbazides, along with some other new substances prepared in the course of the work.

*Paratolylsemicarbazide*,  $\text{CH}_3\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$  [4 : 1].

This compound has been previously described by Pinner (*Ber.*, 1888, **21**, 1221), who prepared it by heating paratolylhydrazine and carbamide, crystallising in leaves, melting at 157—158°, and easily soluble in hot water, less so in cold water, soluble also in alcohol. The properties of our preparation, formed by the action of potassium cyanate on paratolylhydrazine hydrochloride, agreed with those given by Pinner, except in regard to the melting point, which we have observed to be 187—188°.

0.1509 gave 0.3211  $\text{CO}_2$  and 0.0912  $\text{H}_2\text{O}$ . C = 58.03; H = 6.71.

$\text{CH}_3\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$  requires C = 58.18; H = 6.66 per cent.

The acetyl and benzoyl derivatives of paratolylphenylsemicarbazide were prepared by Widman's method.

*Acetyl paratolylsemicarbazide*,  $C_7H_7 \cdot N(CO \cdot CH_3) \cdot NH \cdot CO \cdot NH_2$ , crystallises in colourless, shining plates, which melt at  $212.5^\circ$  and are soluble in hot water, less so in alcohol and ether.

0.1908 gave 34.1 c.c. moist nitrogen at  $14^\circ$  and 734 mm.  $N = 20.29$ .

$C_{10}H_{13}N_3O_2$  requires  $N = 20.28$  per cent.

*Benzoylparatolylsemicarbazide*,  $C_7H_7 \cdot N(C_7H_5O) \cdot NH \cdot CO \cdot NH_2$ , formed colourless, shining leaves melting at  $218^\circ$ .

0.1346 gave 0.3297  $CO_2$  and 0.0690  $H_2O$ .  $C = 66.80$ ;  $H = 5.69$ .

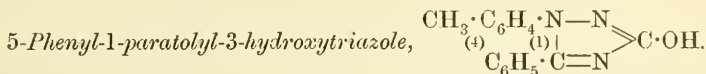
$C_{15}H_{15}N_3O_2$  requires  $C = 66.91$ ;  $H = 5.57$  per cent.

*Paratolylazocarbamide*,  $C_7H_7 \cdot N:N \cdot CO \cdot NH_2$ .

The azocarbamide was prepared from the semicarbazide by the action of potassium permanganate in hot, dilute sulphuric acid; the solution, on cooling, deposited yellowish-red crystals, which, after recrystallisation from hot water, melted at  $142^\circ$ . Paratolylazocarbamide is easily soluble in hot water, alcohol, and ether.

0.1688 gave 37.6 c.c. moist nitrogen at  $15^\circ$  and 748 mm.  $N = 25.66$ .

$C_8H_9N_3O$  requires  $N = 25.76$  per cent.



This oxytriazole was prepared by oxidising an alcoholic mixture of paratolylsemicarbazide and benzaldehyde by means of ferric chloride, and can also be obtained by heating a mixture of paratolylazocarbamide, benzaldehyde, ferrous chloride, and alcohol in a sealed tube at  $120$ — $130^\circ$ . When recrystallised from alcohol, phenylparatolylhydroxytriazole formed colourless, prismatic needles melting at  $242^\circ$ . It is easily soluble in hot alcohol, in dilute alkalis, in warm alkali carbonate solutions, and in hot, concentrated hydrochloric acid, from the latter of which it is precipitated unchanged by the addition of water. The ammoniacal solution, on gently warming, loses ammonia and deposits the oxytriazole in crystalline scales. The alkaline solutions do not reduce Fehling's solution or silver nitrate.

0.1525 gave 0.4004  $CO_2$  and 0.0727  $H_2O$ .  $C = 71.61$ ;  $H = 5.29$ .

0.1728 „ 24.7 c.c. moist nitrogen at  $14^\circ$  and 759 mm.  $N = 16.79$

$C_6H_5 \cdot (C_7H_7)C_2N_3 \cdot OH$  requires  $C = 71.71$ ;  $H = 5.17$ ;  $N = 16.73$  p. c.

The addition of silver nitrate to the ammoniacal solution throws down the silver derivative of phenylparatolylhydroxytriazole as a white,

curdy precipitate ; this, after being dried at the ordinary temperature, loses weight when heated at  $110^{\circ}$ , but the loss does not correspond to any definite molecular proportion of water.

1.0716, dried at  $110^{\circ}$ , gave 0.4264 AgCl. Ag = 29.97.

$C_6N_5 \cdot (C_7H_7)C_2N_3 \cdot OAg$  requires Ag 30.16 per cent.

*Acetylphenylparatolyloxytriazole*,  $C_6H_5 \cdot (C_7H_7)C_2N_3O \cdot CO \cdot CH_3$ , prepared by boiling the hydroxytriazole with acetic anhydride and fused sodium acetate, is easily soluble in ether, alcohol, and glacial acetic acid. When crystallised from dilute alcohol, it formed masses of white, delicate needles melting at  $112-113^{\circ}$ .

0.1447 gave 0.3688  $CO_2$  and 0.0678  $H_2O$ . C = 69.51 ; H = 5.20.

$C_{13}H_{12} \cdot C_2N_3O \cdot C_2H_5O$  requires C = 69.62 ; H = 5.12 per cent.

The acetyl derivative is hydrolysed by boiling potassium carbonate solution and by dilute hydrochloric acid, yielding phenylparatolyloxytriazole melting at  $242^{\circ}$ .

*Benzoylphenylparatolyloxytriazole*,  $C_6H_5 \cdot (C_7H_7)C_2N_3O \cdot C_7H_5O$ , prepared by acting with benzoic chloride on the silver salt, is easily soluble in alcohol, and crystallises from dilute alcohol in thin, shining plates which melt at  $132^{\circ}$ . It is slowly hydrolysed when boiled with potassium carbonate solution.

0.2128 gave 20.6 c.c. moist nitrogen at  $11^{\circ}$  and 775 mm. N = 11.77.

$C_{13}H_{12} \cdot C_2N_3O \cdot C_7H_5O$  requires N = 11.83 per cent.

*Phenylparatolylethoxytriazole*,  $C_6H_5 \cdot (C_7H_7)C_2N_3 \cdot OC_2H_5$  was obtained by the action of ethylic iodide on the silver salt as a yellow, viscid oil which gradually solidified when kept for some time. After being washed on a porous plate with light petroleum, it melted constantly at  $51-52^{\circ}$ . It is easily soluble in alcohol, ether, benzene, and warm light petroleum, separating from the solvent as an oil which gradually solidifies. It is not attacked by boiling acids or alkalis.

0.1728 gave 0.4628  $CO_2$  and 0.0964  $H_2O$ . C = 73.04 ; H = 6.19.

$C_{13}H_{12} \cdot C_2N_3O \cdot C_2H_5$  requires C = 73.12 ; H = 6.09 per cent.

*$\beta$ -Naphthylsemicarbazide*,  $C_{10}H_7 \cdot NH \cdot NH \cdot CO \cdot NH_2$ .

This has been previously prepared by Pinner (*Ber.*, 1888, 21, 1222) by heating  $\beta$ -naphthylhydrazine hydrochloride with carbamide. The product is described as forming thin leaves, which melted at  $225^{\circ}$  and were sparingly soluble in hot alcohol. Hillringhaus (*Ber.*, 1889, 22, 2657) also prepared the substance, making use of the action of potassium cyanate on  $\beta$ -naphthylhydrazine hydrochloride, and described it as forming silky leaves which melted at  $221^{\circ}$  and were

easily soluble in hot alcohol. Using the same method as Hillringhaus, we obtained a product which was easily soluble in hot alcohol, and after repeated recrystallisation melted sharply at 225°.

0.1767 gave 31.9 c.c. moist nitrogen at 15° and 756 mm.  $N = 21.02$ .

$C_{10}H_7 \cdot N_2H_2 \cdot CO \cdot NH_2$  requires  $N = 20.89$  per cent.

*5-Phenyl-1-β-naphthyl-3-hydroxytriazole*,  $C_{10}H_7 \cdot \overset{1}{N} \cdot \overset{3}{N} \begin{array}{l} \nearrow \\ \searrow \end{array} \begin{array}{l} COH \\ C \cdot N \end{array}$

This hydroxytriazole, prepared by oxidising a mixture of benzaldehyde and β-naphthylsemicarbazide, is easily soluble in hot alcohol, from which it crystallises on cooling in almost colourless prismatic needles melting at 274—275°. It is easily soluble in alkalis, insoluble in dilute acids. The alkaline solutions, which are of a deep carmine colour, do not reduce Fehling's solution. The hydroxytriazole separates from its ammoniacal solution on warming.

0.1561 gave 0.4304  $CO_2$  and 0.0646  $H_2O$ .  $C = 75.19$ ;  $H = 4.59$ .

$C_{10}H_7 \cdot (C_6H_5)C_2N_3 \cdot OH$  requires  $C = 75.26$ ;  $H = 4.53$  per cent.

The addition of silver nitrate to the ammoniacal solution threw down the silver derivative as a yellow, amorphous precipitate.

1.1660, dried at 110°, gave 0.4228  $AgCl$ .  $Ag = 27.31$ .

$C_{10}H_7 \cdot (C_6H_5)C_2N_3 \cdot OAg$  requires  $Ag = 27.41$  per cent.

*Acetylphenyl-β-naphthyl-oxytriazole*,  $C_6H_5 \cdot (C_{10}H_7)C_2N_3O \cdot C_2H_3O$ , was prepared by boiling the hydroxytriazole with acetic anhydride and fused sodium acetate. After recrystallisation from a mixture of benzene and light petroleum, it forms grey, transparent, prismatic needles melting at 142—143°, and is easily soluble in ether or benzene, less so in alcohol, and only sparingly in light petroleum. It is hydrolysed by boiling alkalis and dilute acids.

0.1718 gave 0.4587  $CO_2$  and 0.0727  $H_2O$ .  $C = 72.81$ ;  $H = 4.70$ .

$C_{10}H_7 \cdot (C_6H_5)C_2N_3O \cdot C_2H_3O$  requires  $C = 72.94$ ;  $H = 4.56$  per cent.

*Benzoylphenyl-β-naphthyl-oxytriazole*,  $C_6H_5 \cdot (C_{10}H_7)C_2N_3O \cdot C_7H_5O$ , obtained by the action of benzoic chloride on the hydroxytriazole, crystallised from alcohol as a slightly yellow, crystalline powder which melted at 141—142°. It is fairly soluble in hot alcohol, less so in cold alcohol, and only slightly in ether. It is slowly hydrolysed when boiled with a solution of potassium carbonate.

0.2055 gave 19.0 c.c. moist nitrogen at 16.5° and 762 mm.  $N = 10.78$

$C_6H_5 \cdot (C_{10}H_7)C_2N_3O \cdot C_7H_5O$  requires  $N = 10.74$  per cent.

The action of ethylic iodide on the silver derivative of phenyl



naphthylhydroxytriazole yielded a yellow, viscid oil which did not solidify even on prolonged keeping. It was easily soluble in alcohol, ether, benzene, and warm light petroleum. It was not further investigated.

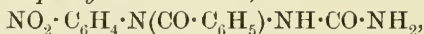
*Metanitrophenylsemicarbazide*,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{NH} \cdot \text{CO} \cdot \text{NH}_2$  [3 : 1].

This was prepared by the action of potassium cyanate on metanitrophenylhydrazine hydrochloride. It crystallises from alcohol in delicate needles which melt and decompose at  $195^\circ$ ; it is easily soluble in hot water or alcohol, but only slightly in boiling ether and benzene.

0.1280 gave 31.8 c.c. moist nitrogen at  $19^\circ$  and 756 mm.  $\text{N} = 28.40$ .

$\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2\text{H}_2 \cdot \text{CO} \cdot \text{NH}_2$  requires  $\text{N} = 28.57$  per cent.

*Benzoylmetanitrophenylsemicarbazide*,



crystallises from alcohol in colourless, shining plates which melt at  $188$ — $189^\circ$ . It is easily soluble in boiling alcohol, almost insoluble in ether and benzene.

0.1907 gave 31.8 c.c. moist nitrogen at  $22^\circ$  and 748 mm.  $\text{N} = 18.58$ .

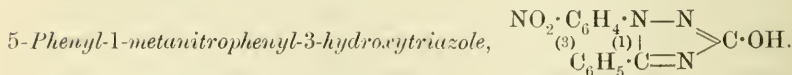
$\text{C}_{14}\text{H}_{12}\text{N}_4\text{O}_4$  requires  $\text{N} = 18.66$  per cent.

*Metanitrophenylazocarbamide*,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N} \cdot \text{N} \cdot \text{CO} \cdot \text{NH}_2$ .

The azocarbamide was prepared by the action of potassium permanganate on the corresponding semicarbazide. The red crystalline product, after recrystallisation from water, melted at  $168$ — $169^\circ$ ; it was moderately soluble in hot water and benzene, readily in boiling alcohol or ether.

0.1870 gave 46.9 c.c. moist nitrogen at  $19^\circ$  and 761 mm.  $\text{N} = 28.85$ .

$\text{C}_7\text{H}_6\text{N}_4\text{O}_3$  requires  $\text{N} = 28.86$  per cent.



This hydroxytriazole was prepared by oxidising a mixture of benzaldehyde and metanitrophenylsemicarbazide, and also by condensing, under conditions similar to those used in previous cases, benzaldehyde with metanitrophenylazocarbamide. Metanitrodiphenylhydroxytriazole separates from alcohol as a yellowish, crystalline powder which melts at  $235^\circ$ . It is easily soluble in hot alcohol and ether, and slightly so in boiling benzene, crystallising out on cooling in clusters of minute needles. It dissolves easily in dilute alkalis and

in warm alkali carbonate solutions; the alkaline solutions do not reduce Fehling's solution. It is soluble in warm concentrated hydrochloric acid, and separates from the solution unchanged on the addition of water.

0.1976 gave 0.4299  $\text{CO}_2$  and 0.0629  $\text{H}_2\text{O}$ .  $\text{C} = 59.33$ ;  $\text{H} = 3.53$ .

$\text{NO}_2 \cdot \text{C}_{12}\text{H}_9 \cdot \text{C}_2\text{N}_3 \cdot \text{OH}$  requires  $\text{C} = 59.57$ ;  $\text{H} = 3.54$  per cent.

On adding silver nitrate to the ammoniacal solution of nitrodiphenylhydroxytriazole, the silver derivative is thrown down as a yellow precipitate, which, after being dried in a vacuum, lost, when heated at  $110^\circ$ , weight approximately equivalent to  $1\text{H}_2\text{O}$ .

1.3275 lost, at  $110^\circ$ , 0.0617  $\text{H}_2\text{O}$ .  $\text{H}_2\text{O} = 4.65$ .

$\text{NO}_2 \cdot \text{C}_{12}\text{H}_9 \cdot \text{C}_2\text{N}_3\text{OAg} + \text{H}_2\text{O}$  requires  $\text{H}_2\text{O} = 4.42$  per cent.

1.2671, dried at  $110^\circ$ , gave 0.4708  $\text{AgCl}$ .  $\text{Ag} = 27.43$ .

$\text{NO}_2 \cdot \text{C}_{12}\text{H}_9 \cdot \text{C}_2\text{N}_3 \cdot \text{OAg}$  requires  $\text{Ag} = 27.76$  per cent.

*Acetylmetanitrodiphenyloxytriazole*,  $\text{NO}_2 \cdot \text{C}_{12}\text{H}_9 \cdot \text{C}_2\text{N}_3\text{O} \cdot \text{C}_2\text{H}_3\text{O}$ , prepared by boiling the hydroxytriazole with acetic anhydride and fused sodium acetate, crystallised from alcohol in shining prisms melting at  $130$ — $132^\circ$ . It is easily soluble in hot ether, alcohol, and benzene, and is quickly hydrolysed by boiling with alkalis or dilute acids.

0.2276 gave 34.5 c.c. moist nitrogen at  $20^\circ$  and 757 mm.  $\text{N} = 17.27$ .

$\text{NO}_2 \cdot \text{C}_{12}\text{H}_9 \cdot \text{C}_2\text{N}_3\text{O} \cdot \text{C}_2\text{H}_3\text{O}$  requires  $\text{N} = 17.28$  per cent.

*Benzoylmetanitrodiphenyloxytriazole*,  $\text{NO}_2 \cdot \text{C}_{12}\text{H}_9 \cdot \text{C}_2\text{N}_3\text{O} \cdot \text{C}_7\text{H}_5\text{O}$ , obtained by the action of benzoic chloride on the silver derivative, crystallised from dilute alcohol in white, delicate needles which melted at  $168^\circ$ ; it was easily soluble in alcohol and ether. Hydrolysis by means of boiling dilute alkalis and acid took place much more slowly than with the acetyl derivative.

0.2101 gave 26.7 c.c. moist nitrogen at  $15.5^\circ$  and 752 mm.  $\text{N} = 14.69$ .

$\text{NO}_2 \cdot \text{C}_{12}\text{H}_9 \cdot \text{C}_2\text{N}_3\text{O} \cdot \text{C}_7\text{H}_5\text{O}$  requires  $\text{N} = 14.50$  per cent.

*Nitrodiphenylethoxytriazole*,  $\text{NO}_2 \cdot \text{C}_{12}\text{H}_9 \cdot \text{C}_2\text{N}_3 \cdot \text{OC}_2\text{H}_5$ , was formed by boiling the silver derivative with ethylic iodide. When recrystallised from alcohol, it separated as yellow, shining needles which melted at  $96^\circ$ , and were easily soluble in alcohol, ether, and benzene. It is not attacked by boiling acids or alkalis.

0.1882 gave 0.4260  $\text{CO}_2$  and 0.0794  $\text{H}_2\text{O}$ .  $\text{C} = 61.73$ ;  $\text{H} = 4.68$ .

$\text{NO}_2 \cdot \text{C}_{12}\text{H}_9 \cdot \text{C}_2\text{N}_3\text{O} \cdot \text{C}_2\text{H}_5$  requires  $\text{C} = 61.93$ ;  $\text{H} = 4.51$  per cent.

XXXVIII.—*Yellow Colouring Principles contained in various Tannin Matters. Part V. Pistacia lentiscus, P. terebinthus, Tamaris africana, T. gallica, Ailanthus glandulosa, Ficus carica.*

By ARTHUR GEORGE PERKIN, F.R.S.E., and PERCIVAL JOHN WOOD.

IN previous communications, it was shown that numerous well-known tannin matters contain yellow colouring principles, which consist either of ellagic acid or members of the quercetin group. During the investigation of Sicilian sumach (Trans., 1896, 69, 1299), the attention of one of us was directed to the excessive adulteration that the commercial article is frequently subjected to, much care on this account being necessary to ensure that the material then examined was a pure sample of the leaves of the *Rhus coriaria*. It was interesting, however, to examine also authentic samples of the adulterants, could these be procured, and the present time was opportune, as we had promise of the aid of Prof. Procter on points of interest with reference to the tanning powers. Owing, apparently, to the desire of the Sicilians to keep the nature of these adulterants secret, attempts to procure them were at first a failure, although application to Sicily was made for us by large and well-known merchants in this country. Ultimately, we were fortunate in obtaining the aid of Mr. P. Gennadius, the Director of Agriculture of Cyprus, who readily supplied us with the required materials, for which our best thanks are due.

Owing to the excessive adulteration of sumach, the quantity exported from Palermo has continually decreased (*Bulletin of Miscellaneous Information*, Royal Gardens, Kew, Nov., 1895, p. 294), and this has been discussed in the *Eco dei Campi. e. dei Boschi* (Rome, Feb. 16, 1897, p. 99) and *Bulletin de la Société nationale d'Acclimation* (Paris, May, 1896). The adulteration consists in grinding with the sumach the leaves of other plants, principally those of *Pistacia lentiscus*, *Ficus carica*, *Ailanthus glandulosa*, *Tamaris africana*, and probably also *Arctostaphylos uva ursi*, and such a mixture, when ground, does not differ in appearance from ground sumach itself. With the aid of the microscope, however, it has lately been found possible to detect this adulteration to some extent, for, of the above plants, the leaves of the *R. coriaria* (sumach) alone are covered with minute, hair-like threads. The difficulty could be readily overcome by importing sumach in the unground leaf form only; any foreign admixture would then be at once visible. It is worthy of remark that Cyprus exports annually much unadulterated sumach in leaves.

*Pistacia lentiscus* (Mastic Tree).\*

The *Pistacia lentiscus* is a small tree about 20 feet high with evergreen leaves, which grows abundantly in most parts of Cyprus, where it is called "shinia." Mastic, or mastick, is the resin of the tree, and this is obtained by making transverse incisions in the bark. For some time, the leaves were exported to England by the Cyprus company, but now are hardly known in this country, although a considerable quantity is consumed at Lyons, in France, as an assistant dyeing material for silk stuffs. About 10,000 tons are exported from Tunis to Sicily annually at a price of 2s. per 100 kilos., and are re-exported from there (as sumach ?) at 3s. 7d. to 5s. 7d. for the same quantity.†

For the sample examined, we are indebted to the kindness of Mr. P. Gennadius, the Director of Agriculture of Cyprus. One thousand grams of the ground leaves were extracted with 10 kilos. of boiling water for 7 to 8 hours, and the light brown extract, which had the characteristic odour of mastic, was treated at the boiling temperature with a solution of 56 grams of lead acetate. The precipitate, which at first was yellow, became nearly colourless on digestion, and this precipitate, which is a lead compound of the tannin matter only, was removed by filtration and washed. On adding lead acetate to the filtrate, a permanent yellow precipitate was formed, and to this, ammonia was added, drop by drop, until the colour no longer increased in intensity; it was then collected, washed, and poured into dilute sulphuric acid, and, after the removal of lead sulphate, the reddish-brown liquid was repeatedly extracted with ether. On evaporating these extracts, a somewhat viscous residue was left, which, on treatment with boiling water, deposited yellow flocks; these were collected (the filtrate A being reserved for examination) and purified by two or three crystallisations from dilute alcohol.

0.1147 gave 0.2365 CO and 0.0345 H<sub>2</sub>O. C = 56.23; H = 3.34.

C<sub>15</sub>H<sub>10</sub>O<sub>8</sub> requires C = 56.60; H = 3.14 per cent.

In this manner, the yield of colouring matter was 1.5 grams, or 0.15 per cent. This was obtained as a lustrous mass of yellow needles, soluble in strong potassium hydroxide solution with a yellow coloration, which, on dilution, changed to a deep green. With aqueous lead acetate, it gave an orange-red precipitate, and reacted readily with mineral acids to form crystalline compounds.

It was acetylated in the usual manner, and the product, after being purified by crystallisation from alcohol, was obtained as a lustrous mass of colourless needles melting at 205—206°.

\* Known in Sicily under the name of "Stinco."

† Pamphlet No. 1, Shinia Leaves, November, 1896, by P. G. Gennadius.



0.1274 gave 0.2665  $\text{CO}_2$  and 0.0482  $\text{H}_2\text{O}$ .  $\text{C} = 57.04$ ;  $\text{H} = 4.20$ .

$\text{C}_{15}\text{H}_4\text{O}_8(\text{C}_2\text{H}_3\text{O})_6$  requires  $\text{C} = 56.84$ ;  $\text{H} = 3.86$  per cent.

From the colouring matter, by fusion with alkali, two products were obtained, melting respectively at  $210^\circ$  and  $238\text{--}240^\circ$ . The former was found to be *phloroglucinol*, and the latter, which gave a blue-black coloration with ferric chloride, was evidently *gallic acid*.

The colouring matter of the leaves of *Pistacia lentiscus* is, therefore, identical with *myricetin*, which has been previously shown to exist in *Rhus coriaria*, or Sicilian sumach (Trans., 1896, 69, 1299), *R. cotinus* (Trans., 1897, 71, 1136), and the *Myrica nagi* (Trans., 1896, 69, 1287).

The filtrate, A, from the crude colouring matter, was treated with sodium hydrogen carbonate and extracted with ether, which removed the last traces of myricetin, and the aqueous liquid was then neutralised with acid, again extracted with ether, and the extract evaporated. The brown, semi-crystalline residue was dissolved in water, and the solution saturated with salt, which caused the separation of a viscous product; this was removed by filtration, and from the filtrate, by means of ether, a crystalline acid was extracted which, after recrystallisation from water, were obtained in a colourless condition.

0.1100 gave 0.2002  $\text{CO}_2$  and 0.0360  $\text{H}_2\text{O}$ .  $\text{C} = 49.63$ ;  $\text{H} = 3.63$ .

$\text{C}_7\text{H}_6\text{O}_5$  requires  $\text{C} = 49.41$ ;  $\text{H} = 3.53$  per cent.

This melted at  $238\text{--}240^\circ$  with evolution of gas, gave with ferric chloride a blue-black coloration, and evidently consisted of *gallic acid*.

Judging from this result, and also from the fact that an aqueous extract of shinia leaves dyes calico mordanted with iron a blue-black shade, it appeared probable that the tannin which they contain was ordinary gallotannin. The deep, red-brown coloration produced on boiling an extract of the leaves with dilute sulphuric acid was, however, a property usually indicative of a catechol rather than a gallotannin; moreover, some qualitative tests which Prof. Procter kindly carried out for us also hardly corroborated this view. Although, as mentioned in previous communications, it is not the intention in these papers to critically examine the tannin contained in the plants under examination, it was necessary, in this case, to make some search for the explanation of the above discrepancies.

*The Tannin.*—An alcoholic extract of the leaves was evaporated to a small bulk, and the deep-green liquid poured into water and repeatedly extracted with ether to remove chlorophyll, wax, and resinous matter. The aqueous solution was now extracted with ethylic acetate until no more tannin was dissolved, and the combined extracts were carefully evaporated; an orange-brown, friable product was thus obtained, readily soluble in water with formation of a pale brown solu-



tion almost free from resinous and suspended matters. To the aqueous liquid, a little salt was added, the small quantity of precipitate thus formed removed, the filtrate extracted with ethylic acetate, and this solution evaporated to a small bulk. The addition of ether caused the precipitation of a trace of a brown product together with some tannin matter, and the now nearly colourless, supernatant liquid was carefully evaporated. A pale, intumescent, friable residue remained, having the appearance of a very pure gallotannic acid, but examination showed that it contained some yellow colouring matter, probably the glucoside of myricetin, which caused it to give, with iron salts, the reactions of a catechol tannin; it yielded, however, no precipitate with bromine water, which is characteristic of the latter. Not having sufficient material to effect its further purification by fractional precipitation with lead acetate, its behaviour with boiling dilute sulphuric acid was studied, for in this way catechol tannins usually form red anhydrides or phlobophanes, whereas gallotannin yields gallic acid. A small quantity of an orange-brown precipitate was formed, which, on investigation, proved to be crude myricetin; this was removed by filtration, the filtrate extracted with ether, and the extract evaporated. The residue, after purification, formed colourless needles melting at  $238-239^{\circ}$ , which had the reactions of *gallic acid*. It thus appeared that the above product was *gallotannic acid* contaminated with the glucoside of myricetin.

The aqueous liquid which had been already extracted with ether still contained a considerable quantity of a tannin and also colouring matter, both probably as glucosides. To remove the latter, lead acetate was added to the solution as long as the precipitate formed was free from yellow colour after digestion at the boiling heat; for it has been shown in these communications that the main bulk of the tannin is thus thrown down before the glucosides of the yellow colouring matters, as these require for their precipitation an excess of the reagent. The precipitate was collected, washed, suspended in water, decomposed with sulphuretted hydrogen, and the lead sulphide removed by filtration. The filtrate, after repeated extraction with ethylic acetate, was evaporated to dryness, and an alcoholic solution of the brown residue treated with ether, until the supernatant liquid was almost colourless. This was decanted and slowly evaporated, there being thus obtained a pale brown, transparent, brittle product, which, when heated to  $100^{\circ}$ , apparently suffered some decomposition, in that it became of a much redder tint. With iron alum, an aqueous solution gave a blue-black coloration, turning greenish black on standing, but with bromine water no precipitate was formed. When digested with boiling dilute sulphuric acid, a reddish-brown precipitate separated, somewhat resembling a red anhydride or phlobophane; this was collected and

washed three or four times with water, in which it was slightly soluble. To obtain some insight into the nature of the tannin, this product was fused with alkali, and this appeared to be a preferable mode of procedure, for should any glucoside of ordinary gallotannic acid originally have been present, which was likely, it must necessarily have been decomposed and the gallic acid thus formed removed by washing with water. The melt, dissolved in water and acidified, emitted a pungent odour of acetic acid, and *phloroglucinol* melting at  $210^{\circ}$ , and *gallic acid* melting at  $238-240^{\circ}$ , were isolated in the usual manner and recognised by the ordinary tests.

It seems apparent, therefore, that the leaves of *Pistacia lentiscus* contain gallotannic acid and a *new tannin* or *tannin glucoside*, yielding the above products on decomposition. As is well known, catechol tannins exist which, on fusion with alkali, form protocatechuic acid and phloroglucinol, of which quebrachotannic acid (Arata, *Jahresbericht*, 1879, 906) is an example, and the above result indicates as probable a natural group of these differing from one another by the number of hydroxyls which they contain. In dealing, however, with amorphous or apparently uncrystallisable substances of this class, a most exhaustive study is required to be sure of a correct interpretation of their properties, and therefore when a larger supply of the raw material is available, it is intended to very thoroughly investigate the nature of this interesting product.

*Tanning Properties.*—According to Sir Thomas Wardle (private communication), the shinia leaves contain 11.29 per cent. of tannin. Under the direction of Professor Procter, a sample of the material employed in the above investigation was analysed by the International Conference method.

Tanning matter .....	11.3 per cent.
Soluble non-tannins.....	22.3   ,,
Insoluble at $60^{\circ}$ F. ....	58.3   ,,
Water .....	8.1   ,,
<hr/>	
100.0	

A good, plump leather is obtained from this material, but of a faintly reddish tint, the result being intermediate in character between those which are given by oak bark and sumach. Although evidently a useful tanning agent for dressing leather, it cannot be employed as a substitute for sumach, when a very light coloured leather is required, but in other respects it has very similar properties.

Experiments on the utility of shinia leaves as an assistant for the fixation of basic colouring matters upon cotton fabrics indicated, as was to

be expected, that they have only half the strength of sumach. When twice the quantity was used, good results were obtained, although the paler shades had a greener and duller character; it seemed, therefore, that shinia leaves would be best employed for the production of the darker tints.

*Tamaris africana.*

This is a shrub or small tree characterised by its twiggy branches and minute scale-like leaves, which are largely used to adulterate sumach, and are known in Sicily under the name of "bruca." In the Kew Report (*loc. cit.*), it is described as having, in lieu of the leaf, prickly little shoots which thickly cover the lesser branches; these are collected, ground, and mixed with the product of the true sumach plant. A very small sample of this material (140 grams) was obtained from Sicily, and although an endeavour was made to procure a larger supply from Tunis, where it is abundant, this met with no response.

For the isolation of the colouring matter, similar means were adopted to those employed with the leaves of the *Pistacia lentiscus*. The ethereal extract, on evaporation, gradually deposited minute, crystalline specks, and these could readily be distinguished in the dry, brown, viscous residue. The addition of hot water caused the separation of a yellow, flocculent precipitate which increased in quantity on cooling; this was collected, dried, and extracted with hot alcohol. A pale brown residue remained undissolved, consisting of the minute crystals above referred to; this was soluble in dilute alkali with a yellow colour, but was only sparingly soluble in the usual solvents. It was found to be *ellagic acid*, for not only did it dye identical shades, but gave, with nitric acid containing nitrous acid, the characteristic reaction of this substance.

The alcoholic extract, after concentration, was treated with water which caused the separation of yellow crystals; these were collected and purified by crystallisation from dilute alcohol. 0.4 gram was thus obtained.

0.0997 gave 0.2214 CO<sub>2</sub> and 0.0345 H<sub>2</sub>O. C = 60.56; H = 3.84.

0.0966 „ 0.2138 CO<sub>2</sub> „ 0.0312 H<sub>2</sub>O. C = 60.36; H = 3.59.

C<sub>16</sub>H<sub>12</sub>O<sub>7</sub> requires C = 60.75; H = 3.79 per cent.

It formed a glistening mass of yellow needles readily soluble in alcohol, and soluble in alkalis with a yellow coloration. With lead acetate, it gave an orange-red precipitate. Treated with mineral acids in the presence of acetic acid, it did not react, at least not so readily as is the case with quercetin and morin, and sufficient material was not available to compare its behaviour in this respect with rhamnetin. It dyed mordanted calico shades of a somewhat similar character to

quercetin, but its properties could not be critically examined in this direction.

No further material from this plant was available for experiment; fortunately, however, the *Tamaris gallica* (see below) contained the same colouring matter, and this enabled us to gain further insight into its nature.

The aqueous filtrate from the above colouring matter was saturated with sodium hydrogen carbonate, extracted with ether to remove phenolic substances, neutralised with acid, and again extracted with ether. A crystalline acid was thus isolated, which, from its melting point and general properties, was found to consist of *gallic acid*.

An aqueous extract of the plant, when digested with dilute sulphuric acid at the boiling temperature, did not develop a red tint, as was the case with the shinia leaves, and which is usually a reaction of catechol tannins; it would thus appear that, in the *Tamaris africana*, only *gallotannic* and *ellagitannic* acids are present.

#### *Tamaris gallica.*

The *Tamaris gallica*, which in appearance closely resembles the *Tamaris africana*, flourishes in Cyprus, where the latter is not found. We are indebted to Mr. Gennadius for a sample of this plant. It weighed 170 grams, 50 of which were reserved for its tannin analysis.

Treated similarly to the *Tamaris africana*, it yielded *ellagic* and *gallic* acids, and contained, therefore, identical tannin matters. The yield of soluble yellow colouring matter was 0.6 gram.

0.0980 gave 0.2175  $\text{CO}_2$  and 0.0342  $\text{H}_2\text{O}$ .  $\text{C} = 60.53$ ;  $\text{H} = 3.87$ .

$\text{C}_{16}\text{H}_{12}\text{O}_7$  requires  $\text{C} = 60.75$ ;  $\text{H} = 3.79$  per cent.

Its properties were identical with the yellow dye-stuff of the allied plant. Its unreactive nature with mineral acids suggested the presence of a methoxy-group, and this was found to be correct.

0.1483 gave 0.0810  $\text{AgI}$ .  $\text{CH}_3 = 3.48$ .

$\text{C}_{15}\text{H}_9\text{O}_6(\text{OCH}_3)$  requires  $\text{CH}_3 = 4.77$  per cent.

The acid residue from this experiment was treated with sodium hydrogen sulphite solution, and the suspended yellow precipitate collected and crystallised from dilute alcohol. The acetyl compound, prepared from a trace of this substance, formed colourless needles melting at  $189-191^\circ$ .

0.0831 gave 0.1820  $\text{CO}_2$  and 0.0277  $\text{H}_2\text{O}$ .  $\text{C} = 59.72$ ;  $\text{H} = 3.70$ .

$\text{C}_{15}\text{H}_{10}\text{O}_7$  requires  $\text{C} = 59.60$ ;  $\text{H} = 3.31$  per cent.

Fused with alkali, the methyl ether yielded an acid melting at  $194-196^\circ$  which, with ferric chloride, gave a green coloration, and was



evidently *protocatechuic acid*. Distinct evidence was also obtained of the presence of *phloroglucinol*.

These results indicate that the colouring matter of the *Tamaris africana* and *T. gallica* contains a *quercetin monomethyl ether*. This does not appear to be either isorhamnetin or rhamnetin, for these methyl ethers of quercetin are distinguished by their sparing solubility in alcohol, and it is therefore most probably a new substance. Whether the product obtained above is homogeneous or contains also quercetin could not be determined; the methoxy-determination favours this supposition, but, on the other hand, low results are sometimes given with this class of substance by Zeisel's method.

On acetylisng a trace of the methyl ether in the usual manner, colourless needles were obtained melting at 169—171°.

Attempts will be made in the ensuing autumn to procure a large supply of the plant for an exhaustive examination of this colouring matter.

A tannin analysis carried out under the direction of Professor Procter gave the following result.

Tanning matter .....	8·4 per cent.
Soluble non-tannins...	26·7   ,,
Insoluble at 60° F. ....	57·7   ,,
Water .....	7·2   ,,
	<hr/>
	100·0

This sample was collected in November, which is not a good season from a tanning point of view, and it is probable, therefore, that the tannin content of that procured from June to August, will be somewhat greater.

#### *Ailanthus glandulosa.*

This is a tree of large size and handsome appearance, bearing numerous pinnate leaves from one to two feet long or more. It is a native of India and China, but is common on the Continent, where it is frequently reared for the shading of public walks. For the sample of leaves we are indebted to Mr. Gennadius, of Cyprus.

The finely ground material was extracted with boiling water, and the extract treated for the isolation of the colouring matter by methods similar to those already described. On evaporating the ethereal extract, a viscous residue was left, interspersed with fine crystals, and from this, on treatment with boiling water, brownish-yellow flocks of a colouring matter separated. These were collected and extracted with boiling alcohol, which left undissolved a brownish, crystalline powder having the dyeing and other properties of *ellagic acid*.



The alcoholic extract, on treatment with boiling water, deposited crystals of a colouring matter, on cooling, but in a very impure condition. The product was therefore poured into water, treated with excess of sodium hydrogen carbonate, the mixture extracted with ether, and the extract evaporated. It was finally purified by crystallisation from dilute alcohol.

0.1068 gave 0.2335  $\text{CO}_2$  and 0.0385  $\text{H}_2\text{O}$ .  $\text{C} = 59.62$ ;  $\text{H} = 4.00$ .

$\text{C}_{15}\text{H}_{10}\text{O}_7$  requires  $\text{C} = 59.60$ ;  $\text{H} = 3.31$  per cent.

It formed a mass of yellow needles, soluble in alkalis with a yellow colour and giving an orange-red precipitate with lead acetate. The acetyl compound crystallised in colourless needles melting at  $189-191^\circ$ .

0.1149 gave 0.2453  $\text{CO}_2$  and 0.0455  $\text{H}_2\text{O}$ .  $\text{C} = 58.22$ ;  $\text{H} = 4.39$ .

$\text{C}_{15}\text{H}_5\text{O}_7(\text{C}_2\text{H}_3\text{O})_5$  requires  $\text{C} = 58.59$ ;  $\text{H} = 3.90$  per cent.

On fusion with alkali, *protocatechuic acid* (m. p.  $194-196^\circ$ ) and *phloroglucinol* (m. p.  $210^\circ$ ) were identified as the principal products. The colouring matter of *Ailanthus glandulosa* is therefore *quercetin*, and to this and ellagic acid, its dyeing properties must be assigned.

The aqueous filtrate from the quercetin was found to contain a large quantity of *gallic acid*, which was identified by its melting point,  $238-240^\circ$ , and general properties. The tannin of the *Ailanthus glandulosa* is evidently gallotannic acid, for the dyeing properties of the leaves with mordants, and the behaviour of the aqueous extract with acids, corroborate this view.

A tannin analysis carried out under the direction of Professor Procter gave the following result.

Tanning matter .....	11.2 per cent.
Soluble non-tannins .....	20.4 „
Insoluble at $60^\circ \text{F}$ .....	60.0 „
Water.....	8.4 „
	<hr/>
	100.0 „

Curiously enough, although so high a percentage of tanning matter is apparently present, leather is scarcely tanned by an extract of these leaves, but is stained a dull dirty colour. They are, therefore, of little utility for tanning purposes, and as an adulterant of sumach would exert a deleterious influence.

#### *Ficus carica.*

For a supply of the leaves of this plant, the common fig tree, we are indebted to the kindness of Mr. P. Gennadius. An aqueous

extract dyed alum mordanted calico but faintly yellow, indicating only a trace of colouring matter, and this was corroborated by experiments carried out according to the methods previously employed. From 2000 grams, only 0.08 gram of a very impure colouring matter was obtained, having dyeing properties analogous to those of quercetin; unfortunately, its identity could not be established, for an attempt to prepare its acetyl derivative failed on account of the impurity present.

The filtrate from the colouring matter contained no gallic acid, and the dyeing property of the leaves with iron mordanted calico indicated an almost entire absence of tannin.

A tanning analysis carried out under the direction of Prof. Procter gave the following result.

Tanning matter .....	1.6 per cent.
Soluble non-tannins .....	27.0 „
Insoluble at 60° F.....	62.4 „
Water .....	9.0 „
	<hr/>
	100.0 „

Skin remained untanned in an extract of these leaves, and was stained a dirty olive colour. It would appear to be an extremely deleterious adulterant of sumach.

#### *Gambuzzo.*

In Sicily, this name is given to the small stalks branching from the main root of the *Rhus coriaria*, which are ground to powder and admixed with sumach. We are indebted to Messrs. Kuypers, Ostler, and Scott, of Hull, for a sample of this material. It has been previously shown by one of us (Trans., 1897, 71, 1136) that the leaves of the *R. cotinus* contain myricetin, whereas it is well known that the stem (young fustic) contains fisetin, and it was thus interesting to determine if this also was the case with the *R. coriaria*.

The stems of the latter possessed but feeble dyeing power, and only after the extraction of much material was a trace of the yellow colouring matter isolated. This on examination was found to be *myricetin*, and not fisetin, for it was readily identified by its characteristic colour reactions with dilute potassium hydroxide solution.

The aqueous filtrate from the colouring matter contained a considerable quantity of *gallic acid*, indicating the presence of gallotannic acid in this portion of the plant also.

The above results show that, whereas the leaves of *Pistacia lentiscus* and the "gambuzzo" contain myricetin, the colouring matter of sumach (*R. coriaria*), the leaves of *Ailanthus glandulosa* and *Tamaris africana* contain respectively quercetin and one of its methyl ethers.

It seemed possible, therefore, that an admixture of the latter with sumach might be detected by the examination of the yellow colouring matter present in the material, for the acetyl compound of such a mixture should have a depressed or indefinite melting point. Experiments carried out in this direction with mixtures of pure quercetin and myricetin, however, hardly favoured the utility of such a method, unless very excessive adulteration had been employed. Thus (a) equal parts of myricetin and quercetin yielded an acetyl compound which, after two crystallisations from alcohol, melted at 195—198°, whereas (b) a similar derivative from three parts of quercetin and one part of myricetin melted at 178—182°. As acetyl myricetin melts at 204—206°, the depression of the melting point to 195—198° in (a) is small, and it became evident that, owing to the more sparing solubility of acetylmyricetin in alcohol, the latter, if present in quantity, could be obtained free from acetylquercetin by frequent recrystallisation.

#### *Broach Leaves.*

These constitute a valuable tanning agent which is employed in South Africa as a substitute for sumach, and in lieu of the leaves of the *Colpoon compressum* (Cape sumach) (Trans., 1897, 71, 1132) which are becoming scarce owing probably to injudicious gathering and lack of care of the plant. Information as to the botanical origin of these leaves is at present lacking, but they are said to be derived from a small shrub flourishing in the same localities and side by side with the *Colpoon compressum*. Mr. R. H. Coaton, to whom we are indebted for our supply of material, 500 grams, promises fuller information on his return to the Cape.

The finely ground leaves were extracted with boiling water, the extract treated with lead acetate solution, and the light yellowish precipitate collected and treated for the isolation of the colouring matter according to the methods previously employed in this paper. The residue from the ethereal extract, when diluted with water, yielded a yellow, flocculent precipitate of the colouring matter, which was purified by crystallisation from alcohol; 0.5 gram was thus obtained.

0.0911 gave 0.1992 CO<sub>2</sub> and 0.0310 H<sub>2</sub>O. C = 59.62; H = 3.78.

C<sub>15</sub>H<sub>10</sub>O<sub>7</sub> requires C = 59.60; H = 3.31 per cent.

It formed glistening, yellow needles closely resembling quercetin in appearance, but soluble in dilute potash with a *deep green coloration*, evidently the result of oxidation; with the concentrated alkali, a yellow solution was obtained, becoming green only on dilution. On acetylation, an acetyl compound was obtained, crystallising in colourless needles and melting at 188—190°, and by fusion with alkali

*protocatechuic acid* and *phloroglucinol* were identified as the main decomposition products.

This colouring matter is evidently identical with that contained in the *Arctostaphylos uva ursi*, a short account of which has been already communicated to the Society (Proc., 1898, p. 104), and which so closely resembles quercetin except in its behaviour towards dilute alkali. In this case also, attempts to remove an impurity having this peculiar property were unsuccessful, and this is remarkable, for if due to such a cause the amount present must be of considerable quantity.

The aqueous filtrate from the colouring matter contained no gallic acid, and the behaviour of the aqueous extract of the leaves towards boiling dilute sulphuric acid, whereby a deep red liquid was produced, indicated the presence of a catechol tannin. This was confirmed by further tests with bromine water and iron alum solution in the usual manner, for these respectively yielded a precipitate and green-black coloration.

Mr. R. H. Coaton has kindly furnished us with the following analysis of this tannin matter.

Tannin .....	19.9 per cent.
Soluble non-tannins .....	14.1 „
Insoluble at 60° F.....	58.4 „
Water .....	7.6 „
	<hr/>
	100.0 „

The galls of *Pistacia terebinthus* were examined for yellow colouring matter. These, which are of a peculiar horn-like shape, are caused by the punctures of insects, and constitute a very valuable tanning material. Owing, however, to an uncertainty in the supply, they appear to have fallen into disfavour in this country.

From 100 grams of these, but a trace of yellow colouring matter was with difficulty isolated, which, judging from its colour reactions with dilute potash solution, appeared to be *myricetin*. Dyeing experiments with mordanted calico also corroborated this view.

An investigation has also been carried out on the colouring matter of "*arbutine*," a ground leaf substitute for sumach. It was found to contain *quercetin*, and, judging from the gallic acid formed during the isolation of the dye-stuff, also gallotannic acid. Unfortunately, the botanical origin of these leaves was not forthcoming on inquiry, and thus no details of the work are at present given. Possibly they are derived from the *Arbutus unedo*, which has been employed in Greece and southern Europe as a tanning material.

In *mangrove cutch*, a well-known tanning material obtained from the *Ceriops candolleana*, yellow colouring matter was found to be

absent. Judging from its resemblance to catechutannic acid, it was examined for catechin, but experiments in this direction were also unsuccessful.

We are much indebted to Prof. Procter for his aid during this investigation, and also for his assistance in obtaining the necessary material.

CLOTHWORKERS' RESEARCH LABORATORY,  
DYEING DEPARTMENT,  
YORKSHIRE COLLEGE.

### XXXIX.—*Isomeric Bornylamines.*

BY MARTIN ONSLOW FORSTER, Ph.D., B.Sc.

HAVING occasion to prepare a specimen of the methyl derivative of bornylamine for purposes of identification, I attempted to devise a process by which bornylamine could be obtained without difficulty.

The existing method of preparing this base, which is due to Leuckart and Bach (*Ber.*, 1887, 20, 104), consists in heating camphor with ammonium formate at 220—240°, when formylbornylamine is produced. In consideration of the fact that both the original process, and the modification introduced by Griepenkerl (*Annalen*, 1892, 269, 347) admit of the manipulation of only four grams of camphor in each operation, it was desirable that a substitute for the method should be found.

It is well known that the oximes of cyclic ketones may be converted into the corresponding amines by reduction with sodium and ethylic alcohol. Leuckart and Bach observed the formation of bornylamine when camphoroxime is submitted to this treatment, but it does not appear that the method afforded satisfactory results, as no details of the experiment are given; it is, moreover, stated that the yield is small, the oxime remaining for the greater part unchanged. It occurred to me to attempt the reduction with amylic alcohol and sodium, and it was found that, by this means, bornylamine may be prepared in almost quantitative amount.

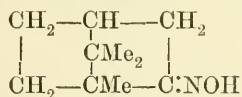
On comparing the product, however, with the compound described by Leuckart and Bach, a marked dissimilarity between the two substances became noticeable. Whereas the latter base melted at 158—160°, and had the specific rotatory power  $[\alpha]_D = -18.6^\circ$ , the bornylamine obtained by the new method melted somewhat indefinitely at 172°, and gave  $[\alpha]_D = -10.3^\circ$ . The divergence appeared still wider when the principal derivatives were prepared and examined, the base obtained



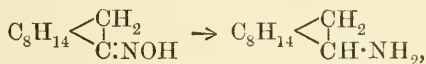
from camphoroxime yielding products which melted several degrees higher than those described by Leuckart and Bach; the acetyl derivative, however, melted several degrees lower than acetylbornylamine. Furthermore, on preparing bornylamine from camphor and ammonium formate, although every endeavour was made to reproduce the conditions described by Leuckart and Bach, I obtained a base which gave  $[\alpha]_D = -16.9^\circ$ , but melted at  $172-173^\circ$ ; the derivatives of this base moreover, resembled those from bornylamine prepared by the new method.

The conflicting nature of these observations seemed to indicate the existence of at least two bases, and an examination of the product from camphoroxime has established the mixed character of the base from this source. It is, in fact, composed of two isomerides having the empirical formula  $C_{10}H_{19}N$ , one of which melts at  $163^\circ$  and has the specific rotatory power  $[\alpha]_D = +45.5^\circ$ , whilst the other melts at  $180^\circ$  and has the specific rotatory power  $[\alpha]_D = -31.3^\circ$ .

It may at first appear singular that the two bornylamines do not exhibit the characteristics of optical antipodes. Consideration of the circumstances attending their production, however, will at once afford an explanation. Adopting Bredt's expression of the constitution of camphor, the oxime is represented by the formula



which contains two asymmetric carbon atoms. Reduction of the oximido-group involves the following change,



by which a third carbon atom is rendered asymmetric. Two compounds might therefore be produced, in one of which the optical influence of this carbon atom is equal and opposite to that which it exerts in the other, but assuming that the influence of the two asymmetric atoms already in the molecule undergoes no modification, the substances thus generated would be incapable of uniting to form an inactive, racemic compound. Moreover, they would not necessarily be produced in equal amounts. Nor is this the case. In round numbers, the mixture obtained on reducing camphoroxime under the conditions finally adopted, contains 60 per cent. of the dextrorotatory base, and 40 per cent. of the lævo-compound.

In view of the fact that these substances are not optical antipodes, one is not justified in distinguishing them as *d*- and *l*-bornylamine, as they are both derived from *d*-camphor. Having found that the base

prepared by the method of Leuckart and Bach is a mixture of the two isomerides in varying proportions, I propose to retain the name *bornylamine* for the dextrorotatory base, and to call the lævorotatory compound *neobornylamine*.

The distinctive character of these two substances is illustrated by the following table.

	Bornylamine.	Neobornylamine.
Base .....	m. p. $163^{\circ}$ ; $[\alpha]_D = +45.5^{\circ}$	m. p. $180^{\circ}$ ; $[\alpha]_D = -31.3^{\circ}$
Hydrochloride .....	infusible below $320^{\circ}$ ; $[\alpha]_D = +22.7^{\circ}$	infusible below $320^{\circ}$ ; $[\alpha]_D = -39.0^{\circ}$
Formyl derivative.	m. p. $93^{\circ}$ ; $[\alpha]_D = -42.1^{\circ}$	m. p. $72-73^{\circ}$ ; $[\alpha]_D = -19.4^{\circ}$
Acetyl derivative...	m. p. $145^{\circ}$ ; $[\alpha]_D = -42.9^{\circ}$	m. p. $143^{\circ}$ ; $[\alpha]_D = -19.5^{\circ}$
Benzoyl derivative.	m. p. $139^{\circ}$ ; $[\alpha]_D = -21.8^{\circ}$	m. p. $130^{\circ}$ ; $[\alpha]_D = -44.7^{\circ}$
Platinochloride ...	m. p. $321^{\circ}$	m. p. $303^{\circ}$
Carbamide ... ..	m. p. $175^{\circ}$	m. p. $169^{\circ}$
Phenylcarbamide...	m. p. $270^{\circ}$	m. p. $254^{\circ}$
Picrate .....	m. p. $256^{\circ}$	m. p. $248^{\circ}$

It will be noticed that, although bornylamine melts at  $17^{\circ}$  lower than neobornylamine, all its derivatives have a higher melting point than those of the isomeride. A corresponding distinction applies to their solubilities, the derivatives of bornylamine being systematically less readily soluble than those of the lævorotatory base. This property is utilised in separating the two isomerides.

A striking parallel with the results described in this paper is afforded by the isomeric menthylamines. Reducing lævorotatory menthoneoxime in alcoholic solution with sodium, Andres and Andréeff (*Ber.*, 1892, 25, 609) obtained a menthylamine boiling at  $205^{\circ}$ , and having the specific rotatory power  $[\alpha]_D = -33.6^{\circ}$ ; by the same method, Wallach and Binz (*Annalen*, 1893, 276, 323) obtained the base with a specific rotatory power  $[\alpha]_D = -38.07^{\circ}$ . When, however, lævorotatory menthone was heated with ammonium formate at  $190-200^{\circ}$ , the formyl derivatives of both lævorotatory and dextrorotatory menthylamine were produced (Wallach and Kuthe, *Annalen*, 1893, 276, 306). Advantage was taken of the greater solubility of the formyl derivative obtained from the lævo-base to separate it from the dextrorotatory modification, from which dextrorotatory menthylamine was obtained as an oil boiling at  $205^{\circ}$ , and having the specific rotatory power  $[\alpha]_D = +14.71^{\circ}$  (*loc. cit.*, 324).

As in the case of bornylamine, the simultaneous production of stereoisomerides here depends on the conversion of a carbonyl radicle into the group  $\text{:CH}\cdot\text{NH}_2$ , a third carbon atom being thereby rendered asymmetric. One point of difference in the circumstances attending the change is noteworthy. Whilst both menthone and camphor are

converted by the agency of ammonium formate at  $200^{\circ}$  into a mixture of dextro- and lævo-rotatory bases, reduction of menthoneoxime yields but one substance, rotating the plane of polarisation in the same direction as the oxime employed; camphoroxime, on the other hand, gives rise to a mixture of the two forms, in which the dextrorotatory modification preponderates, so that in this case the direction of rotation of the main product is opposite to that which the oxime exhibits.

Reference to the above table will show that, whilst the acidyl derivatives of neobornylamine rotate the plane of polarised light in the same direction as the base from which they arise, those of the dextro-rotatory bornylamine are lævorotatory. Moreover, the specific rotatory power of the formyl and acetyl derivatives is more than twice as great, in the same direction, as that of the corresponding derivatives of neobornylamine; the degree of rotation of the benzoyl derivative is, however, only half as great as that of benzoylneobornylamine.

This reversal of sign on the introduction of acidyl groups into the base was quite unexpected, and so far as can be ascertained, a similar case has not been previously observed. With the exception of fenchylamine and the two menthylamines, which have been investigated by Wallach (*Annalen*, 1893, 276, 315), the acidyl derivatives of optically active bases do not appear to have been examined from this point of view. The following table indicates certain regularities in the change of molecular rotation on passing from the derivatives of bornylamine to those of neobornylamine, and optical data of some interest will perhaps be obtained from a study of the higher homologues of the two series under parallel conditions.

	Bornylamine.		Neobornylamine.		Change of [M] <sub>D</sub> .
	[α] <sub>D</sub> .	[M] <sub>D</sub> .	[α] <sub>D</sub> .	[M] <sub>D</sub> .	
Base.....	+45.5°	+69.6	-31.3°	-47.9	117.5
Hydrochloride .....	+22.7	+43.0	-39.0	-73.8	116.8
Formyl derivative.....	-42.1	-76.2	-19.4	-35.1	41.1
Acetyl derivative .....	-42.9	-83.6	-19.5	-38.0	45.6
Benzoyl derivative .....	-21.8	-56.0	-44.7	-114.8	58.8

Although the values here recorded are not strictly comparable, as the concentration of the solution was not the same in the case of each derivative, it is noticeable that the difference between the molecular rotations of the acidyl derivatives of the two series exhibits a gradual increase with increase in the molecular weight; moreover, the difference between the molecular rotations of bornylamine and neobornylamine is almost identical with the difference between the molecular rotations of the hydrochlorides.

## EXPERIMENTAL.

*Reduction of Camphoroxime.*

Seventy-five grams of the oxime dissolved in 750 c.c. of amylic alcohol (b. p. 128—130°) were treated in a reflux apparatus with 75 grams of sodium, which was added in quantities of about 15 grams. The dissolution of the metal occupied about 4 hours, 100 c.c. of amylic alcohol being added towards the end of this period in order to check the separation of sodium amyloxyde. The flask was then removed from the air bath on which the liquid had been boiled, and the temperature having fallen to about 60°, the contents were treated with 450 c.c. of water; the same volume of concentrated hydrochloric acid was next added in small portions to the liquid, which was shaken vigorously after each addition. Amylic alcohol was finally removed by distillation in a current of steam, and on allowing the aqueous residue to cool, bornylamine hydrochloride rapidly crystallised in lustrous needles, the yield of base being practically quantitative.

As already indicated, however, the product consisted of a mixture of two isomerides. In order to separate these bases, advantage was taken of the greater solubility in water of the hydrochloride of neobornylamine. After remaining overnight, the product obtained from 150 grams of camphoroxime in the manner just described was freed from mother liquor with the aid of the filter pump, and recrystallised four times from boiling water, the minimum quantity of the solvent being used every time. Before each crystallisation, a portion of the hydrochloride was treated with caustic soda, and submitted to distillation in a current of steam, the specific rotatory power of a 4 per cent. solution in absolute alcohol of the base from each fraction being then determined. It was found that successive recrystallisations of the hydrochloride had lowered the melting point of the freshly distilled base from 162° to 159—160°, the depression being accompanied by an increase in the specific rotatory power from  $[\alpha]_D = +28.9^\circ$  to  $[\alpha]_D = +45.5^\circ$ ; this value underwent no change on extracting the hydrochloride with ether, in which neobornylamine hydrochloride dissolves more freely than the dextrorotatory salt, and it also remained stationary when the portion undissolved by ether was recrystallised from water. It is, therefore, not unreasonable to suppose that the salt obtained in this manner is the hydrochloride of an individual base.

The acid mother liquor from the original crystals contained neobornylamine hydrochloride. The base liberated from a portion of the liquid melted somewhat indefinitely at 174—176°, and gave the specific rotatory power  $[\alpha]_D = -26.6^\circ$ . In order to isolate the levorotatory



base, the liquid was evaporated on the water bath until it measured 700 c.c., then cooled rapidly, and filtered after an interval of a few hours. The crystals obtained in this way consisted chiefly of sodium chloride (about 200 grams), but on dissolving the salt in water and adding caustic soda, 7 grams of a base were obtained which melted at  $179-180^{\circ}$ ; a 4 per cent. solution in absolute alcohol gave the specific rotatory power  $[\alpha]_D = -31.3^{\circ}$ . The mother liquor from this fraction was reduced to 150 c.c., but the crop of crystals which separated, although amounting to more than 150 grams, yielded scarcely 0.5 gram of neobornylamine; this melted indefinitely at  $160-174^{\circ}$ , and gave the specific rotatory power  $[\alpha]_D = -16.1^{\circ}$ . Finally, the mother liquor was rendered alkaline, and yielded 11 grams of neobornylamine, which melted very indefinitely at  $155-174^{\circ}$ , and gave the specific rotatory power  $[\alpha]_D = -24.3^{\circ}$ .

From this experiment, it appears that, although bornylamine hydrochloride dissolves less readily in water than the salt of the laevorotatory base, the first crop of crystals which separates on evaporating the mother liquor from the dextrorotatory hydrochloride consists entirely of neobornylamine hydrochloride mixed with sodium chloride, the filtrate still containing some dextrorotatory salt. There is, of course, no absolute guarantee that the fraction which gives the specific rotatory power  $[\alpha]_D = -31.3^{\circ}$  represents a chemical individual, although it is highly probable that this is the case, the first crop of crystals from the mother liquor having occasionally yielded a somewhat less, but never a more, active base.

In order to make sure that the change which camphoroxime undergoes is of a purely chemical nature, depending on reduction of the oximido-group, the substance was heated in a reflux apparatus with a boiling solution of sodium amyloxide in amylic alcohol during several hours; on recovering the oxime, however, its optical activity was found to be unimpaired.

### *Bornylamine and its Derivatives.*

*Bornylamine*,  $C_{10}H_{17}\cdot NH_2$ .—Bornylamine is a white, volatile solid, somewhat resembling camphor, and having a faint, pungent odour which suggests that of piperidine. When freshly distilled in a current of steam, it melts at  $159-160^{\circ}$ , but after remaining in the desiccator for several hours, or on sublimation between watch glasses, it melts at  $163^{\circ}$ .

0.1485 gave 0.4275  $CO_2$  and 0.1692  $H_2O$ .  $C = 78.51$ ;  $H = 12.66$ .

0.1980 „ 15.4 c.c. of moist nitrogen at  $10.5^{\circ}$  and 758 mm.  $N = 9.27$ .

$C_{10}H_{19}N$  requires  $C = 78.43$ ;  $H = 12.42$ ;  $N = 9.15$  per cent.



The base dissolves very readily in cold, organic solvents, but is insoluble in water. A solution containing 1.0124 grams dissolved in 25 c.c. of absolute alcohol at  $22^{\circ}$  gave  $\alpha_D = 3^{\circ} 41'$  as the mean of seven concordant readings in a 2-decimetres tube; this corresponds with the specific rotatory power  $[\alpha]_D = +45.5^{\circ}$ .

The *hydrochloride*, which crystallises from water and from alcohol in long, white needles, dissolves freely in these agents and in chloroform, but is only sparingly soluble in ether. It does not melt below  $320^{\circ}$ . The salt is dextrorotatory, a solution of 1.0746 grams in 25 c.c. of absolute alcohol at  $20^{\circ}$  giving  $\alpha_D = 1^{\circ} 57'$  as the mean of four concordant readings in a 2-decimetres tube, whence the specific rotatory power  $[\alpha]_D = +22.7^{\circ}$ .

*Formylbornylamine*,  $C_{10}H_{17} \cdot NH \cdot COH$ .—The formyl derivative was prepared by the action of boiling, anhydrous formic acid, with which the base was heated in a reflux apparatus during several hours; on cooling the liquid, and pouring it into a large volume of cold water, the compound separated in minute, white crystals. It is readily soluble in cold alcohol, and on diluting the hot solution with water, crystallises in leaflets melting at  $93^{\circ}$ .

0.1247 gave 8.2 c.c. of moist nitrogen at  $10.5^{\circ}$  and 758 mm.  $N = 7.84$ .  
 $C_{11}H_{19}NO$  requires  $N = 7.73$  per cent.

Formylbornylamine is scarcely soluble in cold light petroleum, and dissolves but sparingly in the boiling liquid, from which it separates in transparent, rhomboidal plates. Although derived from a dextrorotatory base, the formyl derivative is levorotatory; 0.8918 gram dissolved in 25 c.c. of absolute alcohol at  $20^{\circ}$  gave  $\alpha_D = -3^{\circ} 0'$  as the mean of six concordant readings in a 2-decimetres tube, whence the specific rotatory power  $[\alpha]_D = -42.1^{\circ}$ . This result being quite unexpected, it seemed advisable to ascertain whether treatment with boiling formic acid had exerted any influence on the base besides a chemical one. A specimen of unpurified formylbornylamine having  $[\alpha]_D = -40.0^{\circ}$  was therefore hydrolysed with alcoholic soda; the regenerated base gave the specific rotatory power  $[\alpha]_D = +38.1^{\circ}$ , the calculated value being  $[\alpha]_D = +38.4^{\circ}$ .

*Acetylbornylamine*,  $C_{10}H_{17} \cdot NH \cdot CO \cdot CH_3$ .—The acetyl compound was prepared by boiling for several hours in a reflux apparatus a solution of the base in glacial acetic acid containing a few drops of acetic anhydride; the liquid was then poured into a considerable quantity of cold water, and the acetyl derivative, which separated in small, white leaflets, recrystallised from dilute spirit. It is freely soluble in cold alcohol and other organic solvents excepting light petroleum, in which it dissolves sparingly when hot, crystallising in lustrous, square, transparent plates; the substance softens at about  $140^{\circ}$ , and melts at  $145^{\circ}$ .

0.1972 gave 12.2 c.c. of moist nitrogen at 14° and 766 mm.  $N = 7.34$ .

$C_{12}H_{21}NO$  requires  $N = 7.18$  per cent.

The acetyl derivative dissolves sparingly in boiling water, separating in highly lustrous crystals as the liquid cools. Resembling formylbornylamine, it is laevorotatory, a solution containing 0.7315 gram in 25 c.c. of absolute alcohol at 20° giving  $\alpha_D = -2^\circ 30' 5''$  as the mean of seven concordant readings in a 2-decimetre tube; the specific rotatory power  $[\alpha]_D = -42.9^\circ$ .

*Benzoylbornylamine*,  $C_{10}H_{17} \cdot NH \cdot CO \cdot C_6H_5$ .—Benzoylbornylamine was prepared from the base by the Schotten-Baumann method. It dissolves readily in cold alcohol, separating from the hot liquid on dilution with water; it is insoluble in cold light petroleum, dissolving sparingly in the hot medium, from which it crystallises in lustrous, silky needles. The substance melts at 139°.

0.1920 gave 9.2 c.c. of moist nitrogen at 16° and 773 mm.  $N = 5.67$ .

$C_{17}H_{23}NO$  requires  $N = 5.45$  per cent.

A solution containing 1.0013 grams of the benzoyl derivative in 25 c.c. of absolute alcohol at 20° gave  $\alpha_D = -1^\circ 45'$  as the mean of eight concordant readings in a 2-decimetre tube; this corresponds with the specific rotatory power  $[\alpha]_D = -21.8^\circ$ .

*Bornylamine Platinochloride*,  $(C_{10}H_{19}N)_2, H_2PtCl_6$ .—The salt is very sparingly soluble in hot water and in cold absolute alcohol; it is not freely soluble in boiling alcohol, but dissolves readily in hot alcohol containing hydrochloric acid, from which it crystallises on cooling in transparent, golden, six-sided plates.

0.1632 gave 0.0444 Pt.  $Pt = 27.20$ .

0.4118 „ 0.1122 Pt.  $Pt = 27.24$ .

$(C_{10}H_{19}N)_2, H_2PtCl_6$  requires  $Pt = 27.21$  per cent.

When heated in a capillary tube, the platinochloride begins to darken at about 270°, rapidly becoming black above this temperature; and at 321°, it melts, and undergoes vigorous decomposition.

The *carbamide* of bornylamine is formed on boiling an aqueous solution of the hydrochloride with the calculated amount of potassium cyanate in a reflux apparatus; the filtered liquid deposits the substance on cooling, and after recrystallisation from boiling water, the carbamide is obtained in long, lustrous needles melting at 175°. It is volatile in an atmosphere of steam.

The *phenylcarbamide* rapidly separates in lustrous leaflets on adding an ethereal solution of phenylic isocyanate (1 mol.) to the base dissolved in ether. It crystallises from absolute alcohol in white, silky needles, and melts at 270°, with slight effervescence.

The *picrate* of bornylamine crystallises from alcohol in long, sulphur-yellow, prismatic needles, and melts at  $257^{\circ}$ ; it begins to darken at about  $240^{\circ}$ , and decomposes vigorously at the melting point.

*Neobornylamine and its Derivatives.*

*Neobornylamine*,  $C_{10}H_{17}\cdot NH_2$ .—Neobornylamine closely resembles the dextrorotatory base, remaining as a powder, however, after being kept in the desiccator, which treatment causes the isomeride to become more camphor-like in consistence. It melts at  $180^{\circ}$ .

0.2438 gave 0.7000  $CO_2$  and 0.2689  $H_2O$ .  $C = 78.30$ ;  $H = 12.25$ .

0.2326 „ 17.8 c.c. of moist nitrogen at  $18^{\circ}$  and 778 mm.  $N = 9.04$

$C_{10}H_{19}N$  requires  $C = 78.43$ ;  $H = 12.42$ ;  $N = 9.15$  per cent.

The base is even more freely soluble in organic solvents than bornylamine, and is insoluble in water. A solution containing 1.0033 gram dissolved in 25 c.c. of absolute alcohol at  $19^{\circ}$ , gave  $\alpha_D = 2^{\circ} 31'$  as the mean of eight concordant readings in a 2-decimetre tube, whence the specific rotatory power  $[\alpha]_D = -31.3^{\circ}$ .

The *hydrochloride* is very readily soluble in water and in alcohol, and, on slow evaporation, crystallises in lustrous, white needles; it is freely soluble in chloroform, and also dissolves readily in ether. It does not melt below  $320^{\circ}$ . The salt is levorotatory, a solution containing 0.7340 gram dissolved in 25 c.c. of absolute alcohol at  $22^{\circ}$  giving  $\alpha_D = -2^{\circ} 17'$  as the mean of six concordant readings in a 2-decimetre tube; this corresponds with the specific rotatory power  $[\alpha]_D = -39.0^{\circ}$ .

It is unfortunate that, although the hydrochloride of neobornylamine dissolves more freely in ether than the dextrorotatory salt, the difference cannot be conveniently applied in isolating either base. A specimen of bornylamine hydrochloride, which, on treatment with alkali, yielded a base having the specific rotatory power  $[\alpha]_D = +29^{\circ}$ , was extracted several times with ether. The base liberated from the residue gave  $[\alpha]_D = +32^{\circ}$ , and on evaporating the ethereal extract, treating with alkali, and submitting the product to distillation in a current of steam, a base was obtained which gave the specific rotatory power  $[\alpha]_D = -11^{\circ}$ . In neither case, therefore, was a pure substance obtained.

*Formylneobornylamine*,  $C_{10}H_{17}\cdot NH\cdot COH$ .—The formyl derivative of neobornylamine was prepared in the same way as the compound from the dextrorotatory base; on pouring the formic acid solution into cold water, it separated as an oil, but soon solidified. It is very readily soluble in light petroleum and in alcohol, but crystallises from

dilute spirit in nacreous leaflets melting at  $72-73^{\circ}$ . A solution containing 0.3004 gram dissolved in 25 c.c. of absolute alcohol at  $20^{\circ}$  gave  $\alpha_D = -28'$  as the mean of ten concordant readings in a 2-decimetre tube, whence the specific rotatory power  $[\alpha]_D = -19.4^{\circ}$ .

*Acetylneobornylamine*,  $C_{10}H_{17}\cdot NH\cdot CO\cdot CH_3$ .—The base is not converted into the acetyl derivative under the influence of boiling glacial acetic acid unless a few drops of acetic anhydride are added, and the liquid boiled during several hours in a reflux apparatus; the acetyl derivative is obtained as a crystalline precipitate on pouring the solution into cold water. It dissolves readily in cold alcohol, and on diluting the liquid, separates in leaflets; it is scarcely soluble in cold petroleum, and dissolves but sparingly in the boiling agent, crystallising from it in transparent needles and leaflets melting at  $143^{\circ}$ .

0.1380 gave 8.5 c.c. of moist nitrogen at  $14^{\circ}$  and 766 mm.  $N = 7.30$ .

$C_{12}H_{21}NO$  requires  $N = 7.18$  per cent.

The specific rotatory power was determined in absolute alcohol; a solution containing 0.3202 gram dissolved in 25 c.c. gave  $\alpha_D = -30'$  as the mean of ten concordant readings in a 2-decimetre tube, whence the specific rotatory power  $[\alpha]_D = -19.5^{\circ}$ .

An intimate mixture of the acetyl derivatives of the two bases melts somewhat indefinitely at  $120^{\circ}$ ; repeated crystallisation from petroleum does not raise the melting point of such a mixture above  $125^{\circ}$ .

*Benzoylneobornylamine*,  $C_{10}H_{17}\cdot NH\cdot CO\cdot C_6H_5$ .—The benzoyl derivative of neobornylamine dissolves more freely in boiling petroleum than the compound obtained from the dextrorotatory base, but it is only sparingly soluble in the cold medium; it crystallises from the hot solution in lustrous needles. The substance dissolves readily in cold alcohol, and on diluting the solution with water, separates in glistening white leaflets melting at  $130^{\circ}$ .

0.1662 gave 8.2 c.c. of moist nitrogen at  $12^{\circ}$  and 754 mm.  $N = 5.81$ .

$C_{17}H_{23}NO$  requires  $N = 5.45$  per cent.

A solution containing 0.4564 gram dissolved in 25 c.c. of absolute alcohol at  $20^{\circ}$  gave  $\alpha_D = -1^{\circ} 38'$  as the mean of six concordant readings in a 2-decimetre tube, whence the specific rotatory power  $[\alpha]_D = -44.7^{\circ}$ .

*Neobornylamine Platinochloride*,  $(C_{10}H_{19}N)_2\cdot H_2PtCl_6$ .—The platinochloride of neobornylamine dissolves very readily in hot alcohol, even without the addition of hydrochloric acid, crystallising in aggregates of lustrous, orange leaflets as the liquid cools. It is also soluble in boiling water, separating in yellow crystals from the cold solution.

0.0807 gave 0.0219 Pt.  $Pt = 27.14$ .

$(C_{10}H_{19}N)_2\cdot H_2PtCl_6$  requires  $Pt = 27.21$  per cent.



The salt darkens at about  $270^{\circ}$ , gradually becoming deeper in colour as the temperature rises; it melts and vigorously effervesces at  $303^{\circ}$ .

The *carbamide* of neobornylamine crystallises from boiling water in minute, white needles, and melts at  $169^{\circ}$ . It is volatile in an atmosphere of steam

The *phenylcarbamide* resembles the corresponding derivative of bornylamine, and crystallises from absolute alcohol in slender, silvery needles. It melts at  $254^{\circ}$ , without undergoing decomposition.

The *picrate* of neobornylamine dissolves readily in hot alcohol, and is only moderately soluble in the cold agent. It crystallises in transparent, sulphur-yellow, prismatic needles, and, darkening at about  $230^{\circ}$ , melts and decomposes at  $248^{\circ}$ .

After consideration of the foregoing results, there can be little doubt that the base described by Leuckart and Bach was a mixture of neobornylamine with about 20 per cent. of the dextrorotatory isomeride. In the following table, the melting points recorded by the investigators mentioned are compared with those given in the present paper; the fourth column shows the corresponding melting points observed with the base obtained from camphor and ammonium formate.

	Bornyl-amine.	Neobornyl-amine.	Base from camphor and ammonia formate.	
			L. and B.	F.
Base .....	$163^{\circ}$	$180^{\circ}$	$158-160^{\circ}$	$172-173^{\circ}$
Formyl derivative .....	93	$72-73^{\circ}$	61	$70-72$
Acetyl derivative .....	145	143	141	$132-134$
Benzoyl derivative.....	139	130	131	$138-139$
Carbamide .....	175	169	164	
Phenylcarbamide .....	270	254	248	

The disagreement between the third and fourth columns does not necessarily imply inaccuracy on either side—it is merely due to the fact that the proportion of bornylamine to the isomeride varies according to the experimental conditions. It is difficult, especially by the sealed tube method, to prepare a base of which the specific rotatory power can be foretold with accuracy. As already stated, in repeating the experiment of Leuckart and Bach, a base was obtained which was less strongly levorotatory than their product; on another occasion, however, the substance was considerably more levorotatory, the only



noticeable difference in the conditions of the experiment being one of temperature.

The investigation of bornylamine and its isomeride is being continued.

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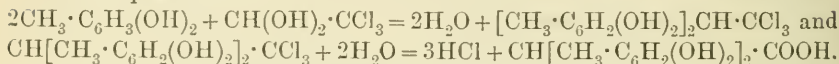
## XL.—*The Condensation of Chloral Hydrate and Orcinol.*

By JOHN THEODORE HEWITT, M.A., D.Sc., Ph.D., and  
FRANK DIXON, B.Sc.

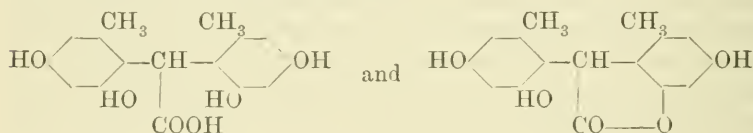
IN two papers communicated to the Society (Trans., 1896, 69, 1265; 1897, 71, 1084), one of the authors has shown, in conjunction with F. G. Pope, that chloral hydrate and resorcinol, when warmed in dilute aqueous solution, condense with formation of the lactone of tetra-hydroxydiphenylacetic acid. The same product had previously been examined by A. Michael (*Amer. Chem. J.*, 1883—1884, 5, 350; 1887, 9, 134) and H. Causse (*Bull. Soc. Chim.*, 1890, [iii], 3, 861); the former investigator had, however, assigned to the substance a wrong molecular formula,  $C_8H_6O_3$ , whilst the latter, although expressing the composition by the formula  $C_{14}H_{10}O_5$ , was incorrect with regard to the constitution. Under these circumstances, it seemed desirable to reinvestigate the substance obtained by Michael and J. P. Ryder by the condensation of chloral hydrate with orcinol, especially as they had assigned to it the *à priori* improbable constitution represented by the formula  $C[CH_3 \cdot C_6H_2(OH)_2]_3 \cdot CH(OH)_2$ .

The result of our work has been to show that the first product of the reaction between orcinol and chloral hydrate in aqueous solution at  $100^\circ$ , potassium hydrogen sulphate being used as a condensing agent, is not, as in the case of resorcinol, a lactone, but a colourless acid, which is only lactonised by heating in the dry state. This acid undoubtedly has the composition  $C_{16}H_{16}O_6$ ; the analyses and molecular weight determination agreeing with this formula. When heated in an indifferent atmosphere to  $150^\circ$ , it loses  $H_2O$ , and is converted into the corresponding lactone,  $C_{16}H_{14}O_5$ ; this lactone contains three hydroxyl groups, as is readily shown by the fact that three acetyl or benzoyl groups may be introduced in the usual way. The benzoate exhibits, however, a peculiar behaviour, in that it readily passes into the dibenzoyl derivative of the acid  $C_{16}H_{16}O_6$  when left in an alcoholic solution containing water: some caution has therefore to be

exercised in the preparation of the tribenzoate. Having ascertained the above-mentioned facts, we were in a position to assign a structural formula to the acid and its lactone. The former is produced according to the equations



Orcinol is 1:3:5-methyldihydroxybenzene, so that the methane carbon atom of the chloral hydrate has the chance of entering the orcinol molecule in the 2, 4, or 6 positions; of these, however, the 2 and 6 positions are equivalent. That it is the 2 or 6 position in which substitution takes place is rendered evident by the fact that, on heating the acid, either by itself or with acetic anhydride or benzoic chloride to their respective boiling points, either the lactone or derivatives of the lactone are produced, and in no case is the formation of xanthene derivatives observed. The acid and its lactone are therefore to be represented by the structural formula

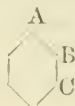


respectively.

The comparative difficulty with which this acid lactonises, and the ease with which the lactone ring is broken, are matters of considerable interest.

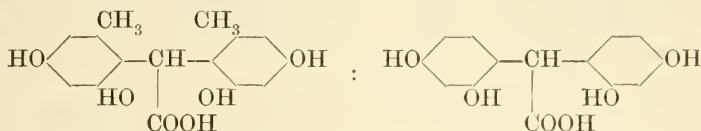
Victor Meyer and his pupils have shown that, if a substituted benzoic acid has two substituent groups in the ortho-positions relatively to the carboxyl group, it can either not be etherified at all or only with difficulty by the ordinary method of heating with an alcohol and a mineral (hydrochloric) acid. Again, Sudborough has observed that 2:6-dibromobenzamide is recovered unaltered after heating for several hours in a sealed tube with 80 per cent. sulphuric acid at 170° (*Trans.*, 1895, 67, 603).

Meyer and Sudborough (compare *Ber.*, 1894, 27, 510, 512, 1580, 3146) are both inclined to attribute this negative behaviour under ordinary conditions of etherification and hydrolysis to want of space within the molecule owing to the volume taken up by the two ortho-substituents. If this be so, it seems feasible to suppose that should A, B, and C represent groups occupying the positions 1, 2, and 3 respectively in a benzene nucleus



group B would exert an outward pressure on groups A and C, and have a tendency to weaken their attachment or to prevent their being increased in volume, although, should A or C be absent, there would be space for both C and B or A and B.

On comparing the constitution of the acid  $C_{16}H_{16}O_6$  with that of the lower homologue  $C_{14}H_{12}O_6$ ,



one can see that, whereas, in the latter case, if lactonisation takes place between carboxyl and hydroxyl and there is in consequence displacement of the methane carbon atom, there is no ortho-substituent on the other side to hinder this motion, in the former case there is the bulkier methyl group standing in the way and tending to resist such displacement.

Similarly, we should expect the influence of these methyl groups to exert themselves in the sense that it would be more difficult to introduce acidyl groups in the place of hydrogen in the case of the ortho-hydroxyl groups than in those in the para-position; and, supposing these groups to be once introduced, for hydrolysis to take place with far greater ease.

Such considerations agree well with the observed facts in that the acid is less readily converted into lactone than the lower homologue; that the lactone is immediately hydrolysed when dissolved in caustic alkalis, and that the tribenzoate of the lactone easily passes into the dibenzoate of the acid in aqueous alcoholic solution.

*Preparation of the Acid  $C_{16}H_{16}O_6$ .*—Two parts of chloral hydrate, 2 parts of potassium hydrogen sulphate, and 3 parts of orcinol are dissolved in 12 parts of water and heated for about 16 hours at  $100^\circ$ ; on cooling, a nearly colourless or pale yellow substance separates in small crystals, which were collected and washed with cold water. On reheating the filtrate with 1 part of chloral hydrate, more of the acid may be obtained; and this operation can be repeated as long as acid of not too dark a colour is deposited. To purify the acid, it may be dissolved in the smallest possible quantity of warm acetone and precipitated as a colourless, crystalline powder by the addition of water; it takes some time to separate completely. It crystallises in microscopic prisms which have a bitter taste. The results of the analysis corresponded with the formula  $C_{16}H_{16}O_6$ .

Calculated ..... C = 63.15; H = 5.26 per cent.

Found..... C = 63.17; 63.59. H = 5.68; 5.17 per cent.

The second analysis was carried out with a specimen which had stood in a desiccator over concentrated sulphuric acid for six weeks ; lactonisation had therefore not proceeded to any appreciable extent.

Michael found  $C=64.58$  and  $64.33$  ;  $H=5.29$  and  $5.34$  ; his substance must therefore have been partially converted into lactone. In conjunction with A. M. Comey (*Amer. Chem. J.*, 1884, 5, 349), he gives the melting point as  $250^{\circ}$ . The corrected melting points for our specimens varied between  $252^{\circ}$  and  $263^{\circ}$ , the latter temperature being the melting point of the corresponding lactone.

The acid is very sparingly soluble in cold water, fairly easily in hot water, and separates out on cooling. It also dissolves in alcohol, benzene, carbon bisulphide, and acetone, but not in light petroleum. The acid dissolves in fairly strong caustic soda solution with a deep blue coloration ; this nearly disappears on moderate dilution with water. Cold, strong sulphuric acid gives no colour reaction.

The molecular weight was found from the boiling point of an alcoholic solution. Alcohol employed 13.96 grams.

0.5703 gram raised boiling point $0.14^{\circ}$ corresponding with mol. wt. 336.
1.0801        "        "        " $0.30^{\circ}$ "        "        "        296.

The calculated molecular weight is 304. We may point out here that Michael's formula corresponds with a molecular weight of 428.

Attempts to prepare salts of the acid were not very satisfactory ; the acid dissolved in a hot solution of potassium carbonate with evolution of carbon dioxide (1 acid : 0.22 potassium carbonate : 10 of water), but nothing separated on cooling ; evaporation did not give a satisfactory result, as the potassium salt is very soluble, and the solution rapidly turned brown. No precipitates were obtained by adding barium chloride, silver nitrate, copper sulphate, ferric chloride, lead acetate or mercuric chloride to this solution.

On treating an aqueous solution of the acid with ferric chloride, a brown precipitate is obtained ; this precipitate is soluble in alkali, and reprecipitated by acids.

*Preparation of the Lactone.*—A weighed quantity of substance was carefully heated in an atmosphere of coal gas for  $1\frac{1}{4}$  hours at a temperature of  $150^{\circ}$ .

0.529, on heating, lost 0.035, corresponding with 6.61 per cent. of water.
0.9528,        "        "        0.0572,        "        "        6.00        "        "

The calculated percentage loss for  $1H_2O$  is 5.92.

The lactone prepared in this way is almost colourless, and melts at  $263^{\circ}$  (corrected). The lactone is apparently immediately hydrolysed on dissolving it in an alkali.

Calculated for  $C_{16}H_{14}O_5$ .... C = 67.13 ; H = 4.89 per cent.  
 Found..... C = 66.94 ; H = 5.01 ..

*Triacetyl Derivative of the Lactone.*—A mixture of 1 part of the acid and 5 parts of acetic anhydride, after being heated for 1 hour in a reflux apparatus, was poured while hot into cold water, and the precipitate recrystallised from ethylic acetate; the substance is thus obtained in small, colourless prisms, melting at  $189^\circ$  (corrected).

Michael and Ryder give the melting point as  $185^\circ$ .

Calculated ..... C = 64.08 ; H = 4.85 per cent.  
 Found .. ..... C = 64.29 ; H = 4.94 ..  
 Michael and Ryder found C = 63.73 ; H = 5.10 ..

The acetate is insoluble in water, and is only sparingly soluble in hydrocarbon solvents; it dissolves, however, in carbon bisulphide, acetic acid, ethylic acetate, and ethylic benzoate. It dissolves on warming with concentrated sulphuric acid, a pale, brown coloration being produced, and on diluting this solution with water, a nearly colourless precipitate is obtained.

*Tribenzoate of the Lactone.*—This was obtained by boiling the acid for about 10 minutes with 10 times its weight of benzoic chloride; after a lapse of a few minutes, no further evolution of hydrogen chloride taking place, the slightly yellow solution of the benzoate in excess of benzoic chloride was poured into light petroleum, whereby it was precipitated in a resinous condition; on pouring off the liquid, adding more light petroleum, and stirring vigorously, the substance is soon obtained in a granular condition. It can be readily purified by dissolving it in ethylic acetate, and adding ethylic alcohol, when it is precipitated as an almost colourless, crystalline powder. It was dried in a vacuum desiccator over sulphuric acid and analysed.

Calculated for  $C_{37}H_{26}O_8$ ... C = 74.25 ; H = 4.35 per cent.  
 Found..... C = 74.43, 75.06 ; H = 4.73, 4.64 per cent.

On heating in a capillary tube, no definite melting point can be observed; the substance sinters at about  $200^\circ$ , and apparently undergoes some decomposition. It is easily soluble in acetone, ethylic acetate, warm ethylic benzoate and chloroform, somewhat soluble in glacial acetic acid and benzene, and apparently quite insoluble in water, alcohol, and light petroleum.

The substance dissolves easily in warm caustic soda solution, the lactone ring being split; it also dissolves in concentrated sulphuric acid, but gives no characteristic colour reaction.

*Dibenzoate of the Acid.*—In preparing the tribenzoate of the lactone, we at first poured our benzoic chloride solution into 90 per cent. alcohol. On one occasion, having to leave the product for 2 days, we



were surprised to find that the substance had entirely dissolved. We were able, however, to obtain a crystalline substance by the addition of water. This, after repeated treatment with dilute alcohol, to remove benzoic acid and ethylic benzoate, was recrystallised from dilute alcohol, and gave, on analysis, numbers agreeing with those of a dibenzoyl derivative of the acid.

Calculated for  $C_{16}H_{14}O_6(C_7H_5O)_2$  C = 70.31 ; H = 4.69 per cent.

Found..... C = 70.92, 70.38 ; H = 4.51, 4.81.

We soon found that it was an acid, and not a lactone, with which we had to deal. The substance dissolves in alcohol very readily ; in this solution, water produces a milkiness which is removed by sodium carbonate solution. The solution of the sodium salt gives precipitates with silver and lead nitrates, the former is, however, fairly soluble in pure water. This dibenzoate melts at  $204^{\circ}$  (corrected). It dissolves readily in alcohol, ethylic acetate, ether, chloroform, benzene, and glacial acetic acid, but is insoluble in water.

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## XLI.—*Sulphonation of Benzophenone and of Diphenylmethane.*

By ARTHUR LAPWORTH, D.Sc.

BENZOPHENONE, in common with all simple benzene derivatives containing the group  $-CO-$  attached directly to the benzenoid nucleus, yields large quantities of *meta*-derivatives when acted on by most substituting agents. Its behaviour in this respect, therefore, is what should, by analogy, be expected, and is in accordance with the rule of Crum Brown and Gibson and with the author's conception (Proc., 1897, 246) of the manner in which *meta*-derivatives are formed.

The behaviour of benzophenone on sulphonation, however, has long been thought exceptional, as the  $\alpha$ -disulphonic acid, the only known acid prepared by direct substitution, yielded parahydroxybenzoic acid only, or almost entirely, when fused with potash (Städel, *Ann.*, 1878, 194, 314), an observation which made it probable that the acid was benzophenoneparadisulphonic acid. Städel states that he observed the production of a small quantity of a second acid, which, however, he did not closely examine.

As the supposition that benzophenone affords no considerable quantity of *meta*-acid involves the idea that its behaviour in this respect is unique, the author took up the study of the question, in the hope that some light might be thrown on the question by indirect

means. It was at first thought probable that the fusion of the sulphonic acid with alkali had resulted in an intramolecular change similar to that which benzene-ortho- and benzene-para-disulphonic acid undergo when subjected to similar treatment, since these acids, as is well known, both yield the metadihydroxy-compound resorcinol. The author's attention was therefore first directed to the possibility either of synthesising the substance from some diphenylmethane acid of known constitution, or of reducing it by some means to the corresponding diphenylmethane acid. These attempts proved fruitless, however, as did all experiments in the direction of preparing its oxime, which it was hoped would undergo the "Beckmann isomeric change," yielding simpler benzene derivatives. No better success was met with when attempts were made to eliminate sulphur dioxide from the disulphonic chloride or bromide, as these substances failed to yield more than a trace of crystalline matter when heated, either alone or with phosphorus pentachloride or pentabromide respectively.

The author finally directed his attention to a careful examination of the acids obtained when the crude products of sulphonation were fused, at as low a temperature as possible, with caustic alkali, in the hope that, by a careful fractionation of the product, metahydroxybenzoic acid might be detected, even if only in relatively small amount. The result was surprising, for not only was metahydroxybenzoic acid found to be the chief product, but, so far as could be ascertained, no great amount of the para-compound was formed. Having succeeded in proving that *meta*-acid was present in the crude sulphonation product, the author repeated the experiment, under several different conditions, employing the purified disulphonic chloride described in the paper; in every case, the only acid found in any considerable quantity was the *meta*-acid.

The difference between the author's result and that of Städel may have been due to one of several causes. Thus, it is not impossible that the conditions employed by Städel in the original sulphonation were different from those used by the author, or that, at the temperature which the author found it necessary to employ during the fusion, the somewhat unstable parahydroxybenzoic acid was destroyed leaving only the stable *meta*-acid. Further, it may be pointed out that the methods employed by Städel for the identification of his substance appear somewhat unsatisfactory; whereas the method employed in this research leaves no room for doubt that the acid obtained was the *meta*- and not the *para*-acid, as the fact that it yielded a tribrominated acid is incompatible with the alternative supposition, for the *para*-acid at once loses carbon dioxide on bromination.

Whatever be the explanation, however, the author's object is accomplished in showing that it is not necessary to suppose that the sulphonation of benzophenone is anomalous. It may still be doubted,

of course, whether it is certain that the disulphonic acid is the heteronuclear dimeta-acid or the parameta-acid; the former constitution, however, appears the more likely.

During the course of the present investigation, several new compounds have been obtained and characterised, more especially certain derivatives of benzophenonedisulphonic acid. The acid itself is presumably the same as that obtained by Städel (*loc. cit.*) and by Beckmann (*Ber.*, 1876, 8, 992); the latter describes its sulphonic chloride, which he found to crystallise from ether in microscopic prisms melting at  $121.5^{\circ}$ . This observation the author has not been able to confirm, as the substance he obtained always formed large prisms or plates melting at  $138^{\circ}$ ; that the substances are identical seems clear from the fact that Beckmann, in one portion of his paper, states that, after carrying the sulphonic chloride through a certain cycle of operations, he recovered it in the form of anorthic crystals melting at  $138^{\circ}$ , and its properties then tally in all respects with those of the author's substance. The observations of Beckmann at once suggest the idea that the difference in melting point was due to dimorphism, a phenomenon which, as is well-known, is not always easy to detect.

A cursory examination of the sulphonic derivatives of diphenylmethane was also made, the action of both chlorosulphonic acid and sulphuric acid on the substance being studied. The results were substantially the same as those obtained by Doer (*Ber.*, 1872, 5, 796), but there is some evidence to show that the products are mixtures of two or more sulphonic acids, as the crude chloride is usually liquid and always difficult to purify, having a melting point which is not easy to obtain constant, even when the product is distinctly crystalline and free from any trace of oily matter. The oxidation of the dipara-acid with permanganate afforded little or no benzophenone acid, as a product was obtained which, on treatment with phosphorus pentachloride, gave almost entirely phosphorus compounds; this behaviour indicating the introduction of hydroxyl groups into the molecule.

#### EXPERIMENTAL.

##### *Sulphonation of Benzophenone.*

Benzophenone is scarcely affected by treatment with chlorosulphonic acid, and the only isolable products are benzophenonesulphone,  $C_{13}H_8SO_3$  (first obtained by Städel on sulphonating with sulphuric acid), and a small quantity of a sulphonic chloride which was not examined. It is, however, quickly attacked by fuming sulphuric acid containing about 15 per cent. of anhydride, and it is advisable to

employ an amount of the latter equal to ten times the weight of the benzophenone used; the whole then becomes sulphonated quickly at about  $90^{\circ}$ , and only a small amount of sulphone is produced.

The product, after dilution, is treated with baryta water until neutral, and the filtrate evaporated and allowed to cool; the crystals which separate are then collected and recrystallised from hot water. The product is nearly homogeneous.

*Barium 3:3' (or 3:4')-benzophenone disulphonate*,  $C_{13}H_8S_2O_7Ba$ , is sparingly soluble in cold water, but dissolves readily in the hot liquid, separating on cooling in flat, shining needles. It is insoluble in alcohol and in acetone. An air-dried specimen was analysed.

0.6581 lost 0.0065 at  $120^{\circ}$  and gave 0.3126  $BaSO_4$ . Ba (in anhydrous salt) = 28.2.

$C_{13}H_8S_2O_7Ba$  requires Ba = 28.7 per cent.

The *potassium* and *ammonium* salts were prepared and found to be excessively soluble in water, but practically insoluble in alcohol. Both crystallise in minute needles.

*Benzophenone-3:3' (or 3:4')-disulphonic chloride*,  $C_{13}H_8O(SO_2Cl)_2$ , which is easily prepared from the potassium salt by means of phosphorus pentachloride at  $100^{\circ}$ , is best purified by shaking its solution in chloroform with water in which a little sodium carbonate is dissolved. It separates from the dried liquid in beautiful, transparent crystals of large size, belonging to the anorthic system, or in curious lenticular plates whose sides appear to be curved owing to the mode of development of the crystal faces. It is practically insoluble in carbon bisulphide, somewhat sparingly soluble in ether and ethylic acetate, but freely in chloroform, hot acetic acid or benzene; from each of these solvents it was deposited in forms crystallographically identical, and in no case was any indication of dimorphism detected. It melts at  $137-138^{\circ}$ .

Attempts were made to eliminate sulphur dioxide from the sulphonic chloride by heating, with the object of obtaining the corresponding dichlorobenzophenone. It slowly evolves sulphur dioxide at  $170-180^{\circ}$ , but chars at the same time, and in no case was it found possible to obtain more than a trace of any crystalline substance in this manner, even when phosphorus pentachloride was present; in the latter case, a small quantity of an amorphous substance was isolated, apparently identical with Beckmann's tetrachloride,  $C_{13}H_8S_2O_4Cl_4$ . Like the other sulphonic derivatives of benzophenone here described, it did not yield an oxime when treated with hydroxylamine.

0.2124 gave 0.1586  $AgCl$ . Cl = 18.5.

$C_{13}H_8S_2O_5Cl_2$  requires Cl = 18.7 per cent.

*Benzophenone-3:3' (or 3:4')-sulphonamide*,  $C_{13}H_8O(SO_2NH_2)_2$ , is sparingly soluble in hot water, benzene, and chloroform, but dissolves



readily in alcohol and acetone. It is best crystallised from hot dilute alcohol, from which it usually separates as an amorphous, white precipitate which suddenly becomes crystalline; it forms thin, shimmering needles melting at  $157^{\circ}$ .

*Benzophenone-3 : 3' (or 3 : 4')-disulphanilide*,  $C_{13}H_8O(SO_2NHC_6H_5)_2$ , is insoluble in hot water, benzene, chloroform, or petroleum, but dissolves readily in ethylic acetate, acetone, and hot alcohol. From ethylic acetate solution, it separates in large, transparent, glistening crystals, or as a sandy powder, and, when heated, becomes opaque at  $167^{\circ}$  and melts at  $177-178^{\circ}$ . *Benzophenone-3 : 3' (or 3 : 4')-disulphopiperidide*,  $C_{13}H_8O(SO_2NC_5H_{10})_2$ , resembles the sulphanilide in solubility, and has the following somewhat remarkable property. When it is dissolved in hot alcohol, it forms a colourless, limpid liquid which when cold sets to a transparent jelly which may be cut with a clean knife; if the jelly be touched with a crystal of the piperidide, however, or if the containing vessel be scratched, the jelly is gradually transformed into a limpid liquid containing crystals of the piperidide in suspension. The crystals of the piperidide obtained by spontaneous evaporation of the cold alcoholic solution are very characteristic, being rectangular plates which are hollowed out at each end nearly to the centre; from ethylic acetate, the substance separates in beautiful, monoclinic prisms very symmetrically developed and with brilliant faces. It melts at  $168^{\circ}$ .

Many attempts were made to reduce one or other of the foregoing benzophenone compounds to the corresponding derivative of diphenylmethane, but all without success. Tin and hydrochloric acid produced no effect whatsoever, and the action of hydriodic acid, where reduction did occur, was to cause complete decomposition or to produce such a mixture that it was impossible to obtain any appreciable quantity of pure reduction product. The attempts were finally abandoned when the result of the fusion had yielded sufficiently significant results.

#### *Fusion of Benzophenonedisulphonic Acid with Alkali.*

The first experiments being made with a view to determine if any meta-acid at all was produced, the whole of the crude sulphonation product was converted into potassium salt, and the liquid, evaporated to a syrupy consistency, was mixed with a very large excess of potassium hydroxide. The whole was then heated in a nickel basin, the temperature being allowed to rise very gradually stage by stage and the mass tested at intervals in order to determine the lowest temperature necessary for the decomposition; at the first indication of sulphite, the temperature was maintained approximately constant until no further alteration took place. The whole was then dissolved in water, acidified, and extracted repeatedly with ether; the latter, on evaporation to



dryness, left a crystalline residue, which, after one crystallisation from water, formed nodular aggregates of needles melting at  $197-199^{\circ}$  and apparently pure and anhydrous. It had, in fact, all the general properties of metahydroxybenzoic acid.

This result being so striking, the products of fusion of the pure sulphonic chloride melting at  $136-137^{\circ}$  were next investigated. As the product again had the characters of nearly pure metahydroxybenzoic acid, the following experiment was made to determine how much para-acid, if any, accompanied it, advantage being taken of the fact that metahydroxybenzoic acid yields a tribrominated acid, whilst the para-acid gives bromophenols only.

The crude ethereal extract of the acidified product of fusion was evaporated to dryness, dissolved in dilute sodium carbonate solution, and the latter extracted repeatedly with ether until the extracts left no appreciable residue on evaporation. The aqueous liquid was then treated with excess of bromine, next decolorised by means of sulphur dioxide, made alkaline with sodium carbonate, and extracted with ether to obtain any bromophenols produced from the para-acid, if that were present. These extracts afforded only 0.2 gram of residue having the odour characteristic of bromophenols, whilst the aqueous solution, after acidification, yielded 7 grams of tribromometahydroxybenzoic acid. This result is sufficient to show that only a very small quantity of parahydroxybenzoic acid could have been formed during the fusion.

That the acid obtained by fusion was identical with metahydroxybenzoic acid was proved by the following observations.

A specimen, dried at  $100^{\circ}$ , gave the following result on analysis.

0.1698 gave 0.3781  $\text{CO}_2$  and 0.0709  $\text{H}_2\text{O}$ .  $\text{C} = 60.7$  ;  $\text{H} = 4.6$ .

$\text{C}_7\text{H}_6\text{O}_3$  requires  $\text{C} = 60.9$  ;  $\text{H} = 4.3$  per cent.

It formed nodular masses of needles when crystallised from water, had a distinctly sweet taste, and melted at  $198-200^{\circ}$ . Microscopically examined, it was indistinguishable from the acid in question ; a mixture of the two had the same melting point as each separately, and when warmed with strong sulphuric acid both gave the same characteristic reddish coloration. The ethylic and methylic ethers, as well as the tribromo-derivatives of the two acids, were prepared and found to be identical.

The tribromo-derivative of the above acid was analysed, after being heated at  $110^{\circ}$  for 6 hours.

0.2179 gave 0.3277  $\text{AgBr}$ .  $\text{Br} = 63.9$ .

$\text{C}_7\text{H}_3\text{Br}_3\text{O}_3$  requires  $\text{Br} = 64.1$  per cent.

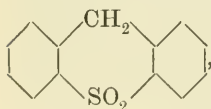
There can be no doubt then, that the acids obtained from the above

benzophenonedisulphonic chloride consist for the most part of meta-hydroxybenzoic acid, and contain only a trace, if any, of the para-acid.

*Sulphonation of Diphenylmethane.*

The products of sulphonation of diphenylmethane were investigated, in the hope of obtaining from the dipara-acid the corresponding derivative of benzophenone for comparison with that obtained from the latter by substitution; and although this was not accomplished, the following facts may be of some interest.

Diphenylmethane is readily sulphonated by means of chlorosulphonic acid; if only one molecular proportion of the latter is employed, the product is a mixture of the mono- and di-sulphonic acids, and much of the hydrocarbon remains unaltered. It was found to be exceedingly difficult to separate the acids, and, as it was foreign to the object of the research, the attempt was not persevered in. When two molecular proportions of the chlorosulphonic acid were used, the product was found to be very similar to that obtained when fuming sulphuric acid was employed, but a considerable quantity of a new substance remained dissolved in the chloroform used after the latter had been extracted with water. This substance is *diphenylmethaneorthosulphone*,



as is shown by the following facts. On analysis,

0.2021 gave 0.2010  $\text{BaSO}_4$   $\text{S} = 13.6$ .

$\text{C}_{13}\text{H}_{10}\text{SO}_2$  requires  $\text{S} = 13.9$  per cent.

When oxidised by a mixture of sulphuric acid and potassium dichromate it afforded some quantity of a compound identical with the sulphone obtained from benzophenone (Städcl, *loc. cit.*), and which is known to be the ortho-derivative, as it is produced when thio-xanthone is oxidised (*Ann.*, 1891, 263, 10).

Diphenylmethanesulphone is readily soluble in chloroform and acetic acid, and crystallises in brilliant, yellowish needles melting at  $169-170^\circ$ .

Some diphenylmethane was sulphonated by means of fuming sulphuric acid; this experiment has already been made by Doer (*Ber.*, 1872, 5, 796) who described some of the salts obtained from the acid produced; doubtless it is the dipara-acid which is the final product, but the author invariably obtained a mixture, as the salts were ill-characterised, and the sulphonic chloride, however carefully made, was contaminated with at least one other substance which lowers its melting

point, and occasionally prevents it from crystallising at all. When the sulphonation has been allowed to go on for a long time (2 days at 80—90°), the chloride obtained is very much more easy to purify; this fact is doubtless due to the gradual change of an ortho-acid into the para-acid, for no large amount of monosulphonic acid appears to be formed at any stage.

The pure sulphonic chloride is best obtained from the crude substance, which is usually liquid, by freezing. The powder which separates may then be collected and recrystallised repeatedly from ethylic acetate mixed with petroleum.

*Diphenylmethane-4 : 4'-disulphonic chloride*,  $C_{13}H_{10}(SO_2Cl)_2$ , is readily soluble in chloroform and ethylic acetate, and separates from the former in bright prisms melting at 124°. When heated at 170—180°, it chars, losing sulphur dioxide, but without affording any crystalline matter.

0.2266 gave 0.1763 AgCl.  $Cl = 19.2$ .

$C_{13}H_{10}S_2O_4Cl_2$  requires  $Cl = 19.5$  per cent.

The *anilide* forms suboctahedral crystals melting at 178°; the *piperidide* is very sparingly soluble in alcohol and ethylic acetate, somewhat readily in acetone, and crystallises from the latter in shimmering leaflets or plates melting at 171—172°.

Attempts were made to oxidise the potassium salt of this sulphonic acid. The salt was dissolved in hot water, and powdered potassium permanganate was gradually added to the solution; when rather less than enough to supply two atomic proportions of oxygen had been added, the colour, which had at first disappeared after each addition, was permanent. The whole was filtered, evaporated to dryness, and treated with phosphorus pentachloride and then with water; the residue was mixed with an equal weight of piperidine, and the mixture of piperidides fractionally crystallised. No trace of any substance having the properties of benzophenonedisulphopiperidide could be detected, and those fractions which approached it in solubility most nearly were found to be phosphorus compounds. This mode of investigation, therefore, was given up as hopeless.

All attempts to oxidise the sulphonamide were equally fruitless, and as the results before mentioned threw entirely new light on the subject, no further examination of the diphenylmethane derivatives was made.

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## XLII.—*Reduction of Bromic Acid and the Law of Mass Action.*

By WINIFRED JUDSON, B.Sc., and JAMES WALLACE WALKER,  
M.A., Ph.D.

WITHIN the last few years the velocities of a large number of chemical reactions have been studied with the purpose of determining the mechanism of their transformations. Many of these have confirmed the theory connecting the velocity of a reaction with the number of molecules participating in it, whilst others have brought some new and remarkable facts to light. The great majority of them, however, only involve a reaction between at most two molecules, and very few of a more complex nature are known in which some subsidiary reaction does not complicate matters to such a degree that they cannot be made to yield simple mathematical results. The reduction of the oxygen acids of the halogens by hydriodic acid is a striking example of this class, and, although it has been studied by numerous chemists, it is only recently that it has been satisfactorily explained by Noyes (*Zeit. physikal. Chem.*, 1896, 19, 599). This is the more remarkable, as we should at first sight consider it to be of a quite simple nature. The experience of all those who have investigated it, however, has led to the opposite conclusion, and although Noyes has shown from Magnanini's determinations that the reaction between hydriodic and bromic acids is one of the *fourth* order, still nothing approaching to an absolute 'velocity constant' has been obtained.

The first reaction of this kind investigated was the interaction of bromic and hydriodic acids by Ostwald (*Zeit. physikal. Chem.*, 1888, 2, 127). He found that the values of  $k$  obtained from the equation

$$k = \frac{1}{t} \frac{x}{A(A-x)}, \text{ instead of being constant, showed a continual decrease}$$

with the progress of the reaction, but he did not attempt to find a solution of the anomaly, as his object then was to determine the accelerating influence of different acids on the velocity of the reaction. The accelerating effect of the different acids employed was, in general, proportional to their affinity constants as determined by conductivity; but there were one or two exceptions, and notable among these was hydrobromic acid, which increased the velocity 10 per cent. more than the value of its affinity constant would have led him to expect. This fact suggests one disturbing influence in the action of hydriodic acid on bromic acid, because, according to the equation  $6\text{HI} + \text{HBrO}_3 = \text{HBr} + 3\text{H}_2\text{O} + 3\text{I}_2$ , hydrobromic acid is formed by the reaction. The



subject was next taken up by Meyerhoffer (*Zeit. physikal. Chem.*, 1888, 2, 585), who attempted to give expression to the other disturbing influence, namely, the retarding action of the liberated iodine. The existence of this retarding effect is much more apparent from the values obtained by another chemist who investigated the subject, namely, Burchard (*Zeit. physikal. Chem.*, 1888, 2, 796). He determined, not only the velocity of the reaction between bromic acid and hydriodic acid, but also employed iodic and chloric acids instead of bromic, and performed his experiments at a large number of different concentrations. The following tables, in which the original concentration of the one is double that of the other, contain some of the results of two of his experiments on HI and  $\text{HIO}_3$ .

C=1.		C=2.	
<i>t</i> in minutes.	Iodine liberated.	<i>t</i> in minutes.	Iodine liberated.
5	3·3 milligrams.	10	38·25 milligrams.
10	5·4           ,,	15	40·88           ,,
20	8·82           ,,	20	42·11           ,,
30	11·13          ,,	30	43·99           ,,
∞	37·96          ,,	∞	75·92           ,,

In the second table it is evident that after 10 minutes the concentrations of the two acids are almost identical with their original concentrations in the first table. If the products of the reaction were without influence on its velocity, therefore, from this point onwards the amount of iodine liberated in a given time ought to be identical with that liberated in Table I; this is evidently not the case. From the middle point in Table II, there is liberated in 5 minutes only 2·63 milligrams of iodine instead of 3·3; in 10 minutes, 3·86 mg. instead of 5·4; and in 20 minutes, 5·74 mg. instead of 11·13. A like result, but more accurate, is got by using the interpolated values obtained from the curves. We mention this method here because it shows the magnitude of the retarding effect, and we shall make use of it afterwards to show that, in the action of bromic on hydrobromic acid, there is no such disturbing influence. Ostwald (*loc. cit.*) arrived at the same conclusion by adding a definite amount of iodine at the commencement. It is evident, therefore, that the action of hydriodic acid on the oxygen acids of the halogens is of too intricate a nature to give any satisfactory numerical results. For this reason, we have selected the reaction between bromic and hydrobromic acids for the subject of a special investigation.

Our first experiments were performed in presence of a large known excess of sulphuric acid, and the method we first employed for determining the amount of bromine liberated after a given time was in



principle the same as that used by Harcourt and Esson (Trans., 1867, 20, 476) in their investigation of the action of hydriodic acid on hydrogen peroxide. Measured volumes of one-fifth normal solutions of potassium bromide and potassium bromate were added to a definite volume of water and, after the addition of 1 c.c. of a decinormal solution of sodium thiosulphate, the beaker containing the solution was placed against a white background and stirred vigorously while 25 c.c. of a 12-times normal solution of sulphuric acid was rapidly run in. The amount of water taken was so adjusted that the volume of the whole was 500 c.c. In one case where the volume was 250 c.c., only 12.5 c.c. of the sulphuric acid solution were added, so that the concentration of the sulphuric acid was practically the same. The oxidation of the thiosulphate by bromine takes place according to the equation  $4\text{Br}_2 + \text{Na}_2\text{S}_2\text{O}_3 + 4\text{H}_2\text{O} = \text{H}_2\text{SO}_4 + \text{Na}_2\text{SO}_4 + 8\text{HBr}$ , and the point of complete oxidation of the thiosulphate was made evident by the appearance of the yellow colour of bromine in the solution, the time was then noted, and 1 c.c. more thiosulphate added. With the concentrations given above, 5 c.c. of potassium bromate solution is in every case equivalent to 7.5 c.c. of the thiosulphate solution; it was therefore possible to obtain 7 readings for 5 c.c. of potassium bromate, 22 with 15 c.c., &c. This method of estimating the amount of bromine is interesting for this reason that, whilst the concentration of bromic acid continually decreases from the reaction  $5\text{HBr} + \text{HBrO}_3 = 3\text{H}_2\text{O} + 3\text{Br}_2$ , that of the hydrobromic acid continually increases, because the 6 atoms of bromine are at once reconverted into hydrobromic acid; the form of the equation connecting the velocity with the concentration must therefore be modified to express this. Taking  $A$  and  $5A$  as the original concentrations of bromic and hydrobromic acid respectively, when 5 c.c. of 0.2 normal bromic, and 25 c.c. of 0.2 normal hydrobromic acids are contained in 500 c.c., after  $x$  grams of bromic acid have disappeared, its concentration will be  $A - x$ , whilst that of the hydrobromic acid will be  $5A + x$ , and the expression for the velocity is  $dx/dt = k(5A + x)(A - x)$ . Under the conditions of the experiment, a very small quantity of hydrobromic acid is therefore capable of transforming an unlimited amount of bromic acid; this circumstance was made use of to obtain a larger number of readings by varying the amount of bromic acid added. A larger amount of bromic acid required, of course, the addition of a proportionately larger quantity of thiosulphate solution, and on this account the error introduced by using 20 c.c. of bromic acid or 30 c.c. of thiosulphate solution is by no means negligible towards the end, although it is practically so during the first third of the reaction. The experiments requiring more thiosulphate were, however, performed to examine the

influence of the thiosulphate itself on the velocity of the reaction. In order to reduce the labour of calculation and to make all our computed values comparable, we have taken the original concentration  $A = 7.5$ , that is, the number of c.c. of decinormal thiosulphate required for 5 c.c. of 0.2 normal bromic acid. The amount of thiosulphate required at any time,  $t$ , therefore represents  $x$ , the quantity of bromic acid which has been reduced up to that time. When varying amounts of hydrobromic acid are added to this same amount of bromic acid, the general equation connecting concentration with velocity is  $dx/dt = k(nA + x)(A - x)$ , which gives on integration

$$k = \frac{1}{(n+1)At} \log_e \frac{nA + x}{n(A - x)}$$

as the value of  $k$ , the velocity constant, or, substituting ordinary for

$$\text{natural logarithms, } k = \frac{1}{0.4343(n+1)At} \log \frac{nA + x}{n(A - x)}.$$

The following tables, I. to V., contain the results of a series of experiments made at  $20^\circ$  with an increasing amount of hydrobromic acid. The concentration in Table VI. is half that in Table III., and in Table VII. is double of that in Table I. Each value of  $t$ , the time, is the mean of a number of observations.  $x$  = c.c. of thiosulphate,  $t$  in minutes.

TABLE I.

$v = 500$  c.c., 5 c.c. KBr and 5 c.c.  $\text{KBrO}_3$ .

$x$	$t$	$k$
1	1.34	0.0133
2	3.0	0.0121
3	4.84	0.0117
4	7.0	0.0113
5	9.65	0.0111
6	13.3	0.0110
7	19.6	0.0115

TABLE II.

$v = 500$  c.c., 10 c.c. KBr and 5 c.c.  $\text{KBrO}_3$ .

$x$	$t$	$k$
1	0.8	0.0115
2	1.77	0.0109
3	2.85	0.0108
4	4.22	0.0105
5	5.87	0.0105
6	8.32	0.0104
7	12.38	0.0111

TABLE III.

$v = 500$  c.c., 15 c.c. KBr and 5 c.c.  $\text{KBrO}_3$ .

$x$	$t$	$k$
1	0.68	0.0089
2	1.49	0.0088
3	2.46	0.0086
4	3.6	0.0086
5	5.09	0.0085
6	7.18	0.0086
7	11.1	0.0089

TABLE IV.

$v = 500$  c.c., 20 c.c. KBr and 5 c.c.  $\text{KBrO}_3$ .

$x$	$t$	$k$
1	0.6	0.0078
2	1.33	0.0073
3	2.15	0.0075
4	3.15	0.0075
5	4.48	0.0074
6	6.39	0.0074
7	10.23	0.0076

TABLE V.

 $v = 500$  c.c., 25 c.c. KBr and 5 c.c.  $\text{KBrO}_3$ .

$x$	$t$	$k$
1	0.48	0.0078
2	1.1	0.0073
3	1.81	0.0072
4	2.67	0.0072
5	3.81	0.0071
6	5.45	0.0072
7	8.68	0.0074

TABLE VI.

 $v = 1000$  c.c. 15 c.c. KBr and 5 c.c.  $\text{KBrO}_3$ .

$x$	$t$	$k$
1	1.5	0.0083
2	3.15	0.0084
3	5.0	0.0085
4	7.4	0.0083
5	10.5	0.0082
6	14.2	0.0087
7	23.4	0.0085

TABLE VII.

 $v = 250$  c.c., 5 c.c. KBr and 5 c.c.  $\text{KBrO}_3$ .

$x$	$t$	$k$	$x$	$t$	$k$
1	0.79	0.0113	5	5.76	0.0093
2	1.82	0.0100	6	7.79	0.0094
3	2.93	0.0096	7	11.33	0.0099
4	4.22	0.0094			

A comparison of these results shows that, from Tables I. and VII. alone, in which the substances are present in the same relative proportions, we might be led to conclude that the reaction is a pure one of the second order, since the value of  $k$  does not vary very greatly from a mean of 0.0100. The same is even more strictly true of Tables III. and VI., where it only varies from 0.0089 to 0.0082. When, however, the values obtained from the other concentrations are also taken into account, it becomes at once evident that the reaction can by no means be looked upon as a simple one and free from disturbing influences, for the value of  $k$  falls continuously with an increasing amount of hydrobromic acid, or, in other words, increases with an increasing amount of bromic acid. This is also apparent from the two following series, where a larger amount of bromic acid was employed with the same amount of hydrobromic acid as in Table I. The equation connecting velocity and concentration is in this case slightly different, that is,  $dx/dt = k(A+x)(nA-x)$  where  $A+x$  is the concentration of the hydrobromic acid after any interval. This equation, when integrated,

gives  $k = \frac{1}{(n+1)At} \log_e \frac{n(A+x)}{nA-x}$  or, employing ordinary logarithms,

$$k = \frac{1}{0.4343(n+1) \times At} \log \frac{n(A+x)}{nA-x}.$$

TABLE VIII.

 $v = 500$  c.c., 5 c.c. KBr and 10 c.c.  $\text{KBrO}_3$ .

$x$	$t$	$k$
1	0.68	0.0126
2	1.53	0.0110
3	2.33	0.0107
4	3.15	0.0104
5	4.05	0.0103
6	4.92	0.0099
7	5.83	0.0098
8	6.82	0.0097
9	7.9	0.0096
10	9.1	0.0095

TABLE IX.

 $v = 500$  c.c., 5 c.c. KBr and 15 c.c.  $\text{KBrO}_3$ .

$x$	$t$	$k$
1	0.43	0.0131
2	0.96	0.0113
3	1.49	0.0107
4	2.00	0.0104
5	2.52	0.0101
6	3.00	0.0100
7	3.52	0.0098
8	4.02	0.0097
9	4.54	0.0095
10	5.07	0.0094

In these, the value of  $k$  does not vary about a mean but decreases continually, so that the mathematical expressions above cannot be regarded as accurate representations of the reaction.

As no other equation of a higher order could be found to give better results, and as the agreement already referred to in series I. and VII., and in III. and VI., where all the reacting substances, namely, bromic acid, hydrobromic acid, and sodium thiosulphate, are present in the same proportions, pointed to the reaction being one of the second order, we were driven to the conclusion that the thiosulphate must be the disturbing agent. In order to test this point, the following experiments were made. Each solution contains the same amount of potassium bromide and bromate, but the thiosulphate was added to them in quantities of 1 c.c., 5 c.c., 10 c.c., and 15 c.c. respectively.  $x$  = c.c. of thiosulphate;  $t$  in minutes.

TABLE X.

 $v = 500$  c.c.; 5 c.c. KBr and 20 c.c.  $\text{KBrO}_3$ .

	1 c.c. at a time.	5 c.c.	10 c.c.	15 c.c.
$x$	$t$	$t$	$t$	$t$
5	2	1.13	—	—
10	3.82	2.57	1.9	—
15	5.68	4.05	—	3
20	7.83	5.48	4.97	—

From this table, it would appear that probably as much of the thiosulphate is directly oxidised<sub>2</sub> by the bromic acid as by the liberated bromine. This reaction between bromic acid and thiosulphate was further proved by adding a drop of the latter to a solution of bromic acid which contained no hydrobromic acid, when bromine was almost instantly liberated. The remarkable observation was made, on carrying the four series included in Table X to completion, that the total time required for the reduction of the whole of the bromic acid present was the same in each case. This is, so far as we are aware, the first

instance which has been observed of a reaction proceeding by two distinct paths to the same end point in the same time, and is doubtless a necessary consequence of the relative changes in concentration of the three reagents under these particular experimental conditions.

After the method described above had been shown to be useless for the object which we had in view, there only remained the more tedious and somewhat less accurate one of titrating the liberated bromine with sodium thiosulphate. In employing this method, it was of course necessary to make up a fresh solution for each reading, as the employment of pipettes would have caused a considerable loss of bromine vapour. We therefore selected a number of 250 c.c. flasks with long necks and well-ground stoppers, introduced into them the potassium bromide, potassium bromate, and sulphuric acid solutions together with the water necessary to make the volume up to 100 c.c., placed them in a thermostat at 20°, and after a definite interval titrated the liberated bromine rapidly with N/100 thiosulphate solution. The 5 c.c. of 12-times normal sulphuric acid solution was, of course, introduced last in order to start the reaction, and the time noted from its addition. The following tables contain the mean results of a large number of experiments performed in the manner described; c.c. of thiosulphate N/100 *t* in minutes.

TABLE XI.

*v* = 100 c.c., 5 c.c. KBr and 1 c.c. KBrO<sub>3</sub>.

c.c. of thiosulphate.	<i>t</i> .	<i>k</i> .
2.3	1	0.00483
3.6	2	0.00421
4.9	3	0.00431
5.8	4	0.00421
6.6	5	0.00419
7.25	6	0.00415
7.75	7	0.00406
8.35	8	0.00419
8.8	9	0.00407
11.3	20	0.00407

TABLE XII.

*v* = 100 c.c., 10 c.c. KBr and 1 c.c. KBrO<sub>3</sub>.

c.c. of thiosulphate.	<i>t</i> .	<i>k</i> .
4.2	1	0.00471
6.6	2	0.00442
8.35	3	0.00433
9.8	4	0.00443
10.75	5	0.00436
11.6	6	0.00442
12.3	7	0.00452
12.8	8	0.00483

TABLE XIII.

*v* = 100 c.c., 10 c.c. KBr and 2 c.c. KBrO<sub>3</sub>.

c.c. of thiosulphate.	<i>t</i> .	<i>k</i> .	c.c. of thiosulphate.	<i>t</i> .	<i>k</i> .
8.1	1	0.00493	18.0	5	0.00400
13.0	2	0.00510	19.4	6	0.00407
14.8	3	0.00433	20.8	7	0.00431
16.5	4	0.00407	21.7	8	0.00436



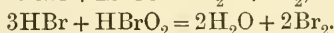
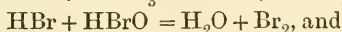
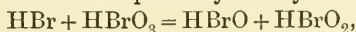
In order to make these tables comparable with the former series, the observed readings must be multiplied by 5, since only 100 c.c. are employed, and divided by 10, because N/100 thiosulphate is used for titration instead of decinormal. If  $A$  is taken equal to 7.5 as before, the observed readings must, therefore, be divided by 2, and the equations to be employed are

$$\text{For XI.} \quad k = \frac{1}{5t} \cdot \frac{x}{A(A-x)}.$$

$$\text{For XII.} \quad k = \frac{1}{0.4343 \times 5 \times t} \log \frac{2A-x}{2(A-x)}.$$

$$\text{And for XIII.} \quad k = \frac{1}{10t} \cdot \frac{x}{A(2A-x)}.$$

These are all equations of the second order, and an examination of the values of  $k$  shows an agreement which is remarkable, considering the comparative crudeness of the experimental method. It is also a much lower number than that obtained by the previous experimental method, showing the great influence of the thiosulphate on the velocity of reaction. In strong sulphuric acid solution, the reaction between bromic and hydrobromic acids is, therefore, without doubt a reaction of the second order. The question as to how this is possible is best answered, as Noyes has pointed out, by assuming that the reaction takes places in different stages, some of which are infinitely quick compared with the others. For example, we may assume that the first stage consists in the formation of bromous and hypobromous acids, which are then at once decomposed by the hydrobromic acid, thus.



If this were so, we should expect to find in the light of the ionic theory that the reaction, which in the presence of a large excess of sulphuric acid is bimolecular, in its absence is of a higher order, probably quadrimolecular, because not only do the Br and BrO<sub>3</sub> ions decrease in number, but the hydrogen ions also decrease from the formation of the two weak acids HBrO<sub>2</sub> and HBrO. This expectation was completely fulfilled by an examination of the reaction velocity between hydrobromic and bromic acids in the absence of sulphuric or any other strong acid.

A pure, normal hydrobromic acid solution was prepared by distilling ordinary hydrobromic acid, and diluting it to the requisite volume, and a solution of pure bromic acid was made by digesting pure barium bromate with dilute sulphuric acid at a low temperature until neither sulphuric acid nor barium chloride gave any precipitate. The strength of the solution was determined by adding excess of standard soda solution and titrating the excess with standard hydrochloric acid, using

litmus as indicator; it was then made up exactly to  $N/5$ . In performing the experiments on the velocity of the reaction, water and the mixture of the acids were used in volume sufficient to give 100 c.c. or 150 c.c., and the free bromine was estimated by an approximately  $N/100$  thiosulphate solution. The time was noted from the addition of the hydrobromic acid, which was introduced from a fast-running pipette; the experiments were carried out at a temperature of  $25^{\circ}$ . It was found by special experiments, in which an excess of sulphuric acid was added, that the total amount of bromine was equivalent to 77 c.c. of thiosulphate solution. This value represents  $A$  in the equations given below, and  $x$  is the observed amount of thiosulphate required in any particular observation.

TABLE XIV.

$v=100$  c.c., 5 c.c. HBr and 5 c.c.  $HBrO_3$ .

c.c. of thiosulphate. $t$ .			c.c. of thiosulphate. $t$ .		
		$k$ .			$k$ .
6.8	2	0.000000117	25.1	15	0.000000110
11.6	4	0.000000115	28.7	20	0.000000111
15.1	6	0.000000111	34.0	30	0.000000115
18.1	8	0.000000112	37.7	40	0.000000119
20.25	10	0.000000109	41.8	60	0.000000115
23.75	13	0.000000114			

TABLE XV.

$v=150$  cc., 5 c.c. HBr and 5 c.c.  $HBrO_3$ .

c.c. of thiosulphate.	$x$ .	$t$ .	$k$ .
5.05	3.37	4	0.000000139
8.20	5.47	8	0.000000124
10.8	7.2	12	0.000000118
15.5	10.33	20	0.000000119
19.9	13.27	30	0.000000119
27.65	18.44	60	0.000000115
36.0	24.0	120	0.000000116

In Table XV., the concentration is only two-thirds of that in XIV., so that  $A$  must be taken as 51.33, and  $x$  as two-thirds of the observed reading. It was, of course, necessary to determine whether the reaction proceeds to an end in the absence of sulphuric acid, or if there is an equilibrium point due to the action of [the liberated bromine on the water, such as is generally supposed to take place. For this purpose, we introduced the reagents in the proportions and quantities given above into flasks which were at once sealed, and allowed to stand for several days at  $25^{\circ}$  before titration. The results show that most of the bromic acid is reduced, but they do not exclude the formation of

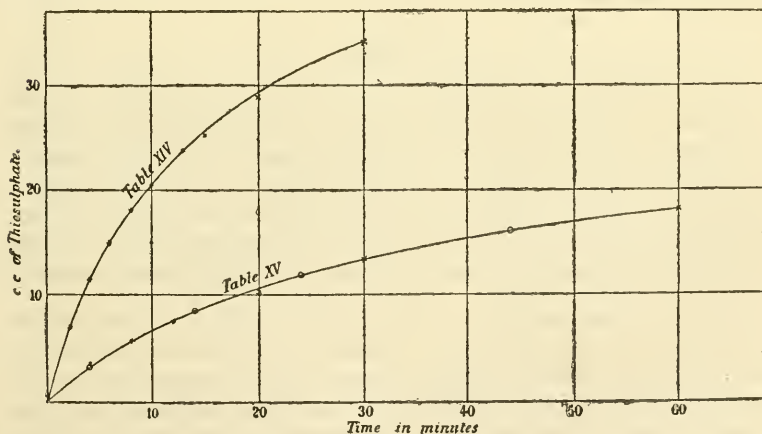
hypobromous acid, which may possibly be readily titrated by thio-sulphate.

$v=100$ c.c., 5 c.c. HBr and 5 c.c. $\text{HBrO}_3$ .		$v=150$ cc., 5 c.c. HBr and 5 c.c. $\text{HBrO}_3$ .	
c.c. of thiosulphate.	$t$ in days.	c.c. of thiosulphate.	$t$ in days.
70	7	67	9
71	11	69.8	18
72.5	20		

An investigation of the curves of these two velocities, however, makes it clear that the backward reaction of bromine on water must be so slight as to be negligible. When one-third of the stronger solution is decomposed, it evidently has the same concentration as the more dilute does at the commencement, except that there is bromine present. If from this point onwards, therefore, there is the same amount of bromine liberated in the same time, the bromine can have no disturbing influence whatever. This point, namely, 25.7, is found from the curve to be reached in 16 minutes, and the values to be tested are therefore

c.c. thiosulphate.	$t$ in minutes.
3.0	4
8.3	14
12.0	24
16.1	44

These points are indicated by a circle upon the curve, and the curve passing through them is found to coincide exactly with that representing the values in Table XV.



After having shown that there is no equilibrium point, the determination of the order of the reaction is quite simple. The method is

described fully in *Studien zur Chemischen Dynamik*, by Cohen, page 106. Two solutions are taken containing the reagents in equivalent quantities as above, but of different concentration,  $c_1$  and  $c_2$ , and the times,  $t_1$  and  $t_2$ , necessary for the transformation of the same fraction of both are determined, by substituting these values in the equation

$$n = 1 + \log \frac{t_1}{t_2} / \log \frac{c_2}{c_1}$$

the value of  $n$  in the equation  $dc/dt = kc^n$  is obtained.

By interpolation, it is found from the curves that the time necessary for the decomposition of one-third of the solution whose concentration is 77 is 15 minutes, whilst the solution of concentration 51.33 requires 50 minutes. Substituting these experimental values, we find  $n = 1 + \log 3.333 / \log 1.5 = 1 + 2.97 = 3.97$ .

This is as close an approximation to 4 as could be desired, and the reaction must, therefore, be one of the fourth order. In order to calculate the value of the velocity constant, since the substances are present in equivalent, not molecular, quantities, and since an equivalent of each disappears simultaneously, we may call  $A$  the initial concentration of both bromic and hydrobromic acid, and the equation connecting velocity with concentration is  $dx/dt = k(A - x)^4$ , which gives, on integration,

$$k = \frac{1}{3t} \left[ \frac{1}{(A - x)^3} - \frac{1}{A^3} \right]$$

The values obtained for  $k$  by means of this equation in tables XIV. and XV. are quite satisfactory; there can, therefore, be no doubt that when the pure acids are allowed to act on each other, the reaction is one of the fourth order.

### Conclusion.

As has been already mentioned, Noyes (*loc. cit.*) has pointed out the mechanism when hydriodic acid is the reducing agent, and a similar one must hold in the case of hydrobromic acid. Since that stage of the reaction, which requires a measurable time for its completion, is one of the fourth order, four individuals must take part in it, or, according to van't Hoff's thermodynamic deductions, four 'osmotic units' must be simultaneously transformed. This is clearly expressed by the ionic equation  $2\overset{+}{\text{H}} + \overset{-}{\text{Br}} + \overset{-}{\text{BrO}}_3 = \text{HBrO} + \text{HBrO}_2$  where the four individuals, two hydrogen, one bromine, and one bromate ion, are converted into the substances hypobromous and bromous acids which, like the weak acids, hypochlorous, boric, and carbonic, are very lightly ionised. This conclusion is supported by the result obtained in presence of a large excess of sulphuric acid. There the number of hydrogen ions is so large that they relatively undergo no change of

concentration. This is expressed by the equation  $\propto \overset{+}{\text{H}} + \overset{-}{\text{Br}} + \overset{-}{\text{BrO}_3}$   
 $= \overset{+}{\text{H}} + \text{HBrO} + \text{HBrO}_2$  or  $\overset{-}{\text{Br}} + \overset{-}{\text{BrO}_3} = \text{HBrO} + \text{HBrO}_2$ , and in accordance with this we find that in presence of a large excess of sulphuric acid the reaction is bimolecular. The velocity when pure bromic and hydrobromic acids are used is therefore directly proportional to the concentrations of the bromate and bromine ions, and proportional to the square of the concentration of the hydrogen ions. This result has already been deduced by Noyes for the reduction of bromic acid by hydriodic acid, and therefore the gradual formation of hydrobromic acid in the latter reaction can exercise but little disturbing influence. We should expect, therefore, the reduction by hydrobromic acid to be much slower than by hydriodic acid. The following calculation shows that this is so. Ostwald found that in a solution which contained 0.2389 gram  $\text{HBrO}_3$  per litre, 0.0846 gram was reduced in 81 minutes at  $25^\circ$ . Substituting these values for  $A$ ,  $x$ , and  $t$  in the equation  $k = \frac{1}{3t} \left[ \frac{1}{(A-x)^3} - \frac{1}{A^3} \right]$ , the value of  $k$  is found to be 0.818.

In the experiment with hydrobromic acid given in Table XIV., the original concentration of bromic acid is 1.29 grams per litre, and after 15 minutes 0.4205 gram has been reduced. This gives 0.023 as the value of  $k$ . This number is not, however, directly comparable with Ostwald's, because the solution only contains 5 molecules of  $\text{HBr}$  to 1 of  $\text{HBrO}_3$ , whilst his contains 6 molecules of  $\text{HI}$  to 1 of  $\text{HBrO}_3$ . It must therefore be multiplied by  $5/6$ , the ratio of the halogen ions, and also by  $36/49$ , the square of the ratio of the hydrogen ions. The result is that  $k = 0.014$ . Hence the reduction by hydriodic acid takes place  $818/14 = 58.4$  times as fast as the reduction by hydrobromic acid, when they are present in equivalent quantities. The slow formation of the latter, therefore, in no way vitiates the conclusions drawn by Noyes from a study of the reaction between bromic and hydriodic acids.

This deduction receives confirmation from the values obtained by Ostwald (*loc. cit.*) in his investigation on the accelerating influence of different acids on the velocity of the reduction of bromic by hydriodic acid. He found that when no other acid was added, 164 minutes were required for the reduction of a definite amount of the bromic acid. 36.6 minutes only were required when a quantity of hydrochloric acid equivalent to the hydriodic acid was added, and 33.8 minutes when a similar quantity of hydrobromic acid was added. We have satisfied ourselves that hydrochloric acid, if it reduces bromic acid at all under the conditions he employed, does so extremely slowly; the whole acceleration which it produces is therefore due to the increase in number of the hydrogen ions. There is the same increase when



hydrobromic acid is added, due to the same cause, for the two are almost equally dissociated, but a further acceleration of 2·8 minutes due to the action of the bromine. Could the same amount of bromine ions, therefore, be added without hydrogen ions, the time required would be 161·2 minutes, therefore the velocity of the reduction by hydriodic acid is  $164 \div (164 - 161\cdot2) = 58\cdot6$  times greater than by hydrobromic acid, a value in almost perfect agreement with that obtained by the former method.

In conclusion, we wish to express our thanks to Professor Ramsay, who proposed the research, and has given us much valuable advice during its progress.

UNIVERSITY COLLEGE, LONDON.

### XLIII.—*The Drying of Ammonia and Hydrogen Chloride.*

By H. BRERETON BAKER, M.A.

IN 1894, a paper was published in the Journal of the Society in which, among several other instances of the effect of moisture on chemical change, I described some experiments which showed that ammonia and hydrogen chloride, when dried by phosphorus pentoxide, do not combine, and that ammonium chloride, when carefully dried, does not dissociate at the boiling point of mercury. In a recent paper by Herr Gutmann (*Annalen*, 1898, 299, 3), these conclusions have been called in question. The experiments made by Herr Gutmann seemed to have been done with so much care that, although I had no shadow of doubt about a result which I have obtained so often, I thought it worth while to repeat some of these experiments, with the view of finding out, if possible, how it came about that our results were so different.

The main contention on his part is that the drying of ammonia and hydrogen chloride cannot be effected by phosphorus pentoxide, since both gases are absorbed by that substance in a shorter time than is necessary to dry them. I mentioned in my previous paper that I had noticed an absorption of ammonia gas by phosphorus pentoxide when the preliminary drying had been badly done, but that this action was not necessarily fatal to the success of the experiment, since the substance formed (diamidopyrophosphoric acid, Gladstone, *J. Chem. Soc.*, 1868, 21, 64), would serve itself as a drying agent, so that if excess of ammonia were added until the action was at an end the ammonia could be obtained sufficiently free from moisture not to combine with dried hydrogen chloride. I never felt, however, com-

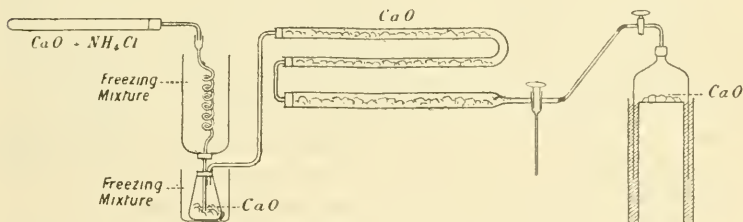
plete confidence in the success of an experiment in the course of which this action took place, and in by far the majority of the experiments the phosphorus pentoxide was apparently unaltered in both the gases. Herr Gutmann, however, describes a rapid absorption of gas in all his experiments, although his preliminary drying of the gases seemed to have been most carefully done. In the three experiments which he quotes, the absorption of ammonia gas by phosphorus pentoxide was measured by the rise of mercury in a tube in which the gas was in contact with the drying agent. His results are as follows.

	Time of contact.	Rise of mercury.
I.	16 hours	613 mm.
II.	12 hours	421 mm.
	36 hours	673 mm.
III.	12 hours	420 mm.
	36 hours	671 mm.

The difference between these results is accounted for by the preliminary drying being different.

I therefore proceeded to investigate the absorption of ammonia, and as the method of preliminary drying of the gas seems to me rather better than Herr Gutmann's, I give a complete description of it.

FIG. 1.



The ammonia was obtained from ammonium chloride, which had been prepared by Stas's method for my former experiments, mixed with lime obtained by igniting precipitated calcium carbonate with a small quantity of sugar. The gas was passed through a worm tube cooled by a freezing mixture of ice and salt into a flask containing lime cooled in a similar way. It was then passed through three long drying tubes containing pieces of lime which had been ignited in a crucible under a layer of powdered lime to prevent the absorption of sulphur from the furnace gases. The gas, collected in a gas-holder containing lime standing over re-distilled and freshly boiled mercury, was left for several days in order to allow of the maximum absorption of water vapour by the lime. The mere passage of a gas through tubes containing a drying agent, especially when this is a solid, cannot

be any guarantee of the removal of moisture. When one considers that in such experiments as have been made on the influence of moisture on chemical action, a mere trace of water is in most cases sufficient to bring about the action, the long continued contact of the drying agent with the gas cannot be too strongly recommended.

In my first experiment on the rate of absorption of dried ammonia gas by phosphorus pentoxide, a long tube provided with a bulb of about 200 c.c. capacity was dried by heating it nearly to the melting point of the glass for 3 hours while a current of air dried by passing through three long tubes of strong sulphuric acid was drawn through it. The phosphorus pentoxide, sealed up in a thin glass tube, was introduced into the bulb, and the apparatus was then filled with ammonia gas by exhausting it and connecting it with the mercury gas-holder in which the gas had been standing over lime. On allowing the bulb to stand over dried mercury and breaking the inner tube of phosphorus pentoxide, the absorption at once began, quickly at first and afterwards more slowly, but in five hours it was almost complete. On reviewing the whole experiment, I could not at first see how a result so different from most of the others I had obtained had come about; the gas had been actually prepared from portions of the same materials, and the drying both of the gas and the tube had been conducted with as much care. The only difference must have been in the phosphorus pentoxide. In the former experiments, I had always tested the drying agent for the three impurities most to be feared in such experiments, namely, the trioxide and tetroxide of phosphorus, and metaphosphoric acid, and when any appreciable proportion of impurity was present, the pentoxide was purified by distillation in a current of dried air. In this new experiment, this precaution had been neglected, and it was found on testing the pentoxide used that it was free from the lower oxides, but on heating at about  $400^{\circ}$  in a current of dried air, it left a very large residue consisting of metaphosphoric acid. In six later experiments, in which the distilled pentoxide was used, I found that it is practically without action both on ammonia and on hydrogen chloride. Ammonia has been left over mercury in contact with phosphorus pentoxide for ten days without a diminution of pressure of more than 10 millimetres, and hydrogen chloride previously dried by standing over re-distilled sulphuric acid in a gas-holder, after being for three weeks in contact with phosphorus pentoxide, showed a diminution of pressure of only 30 mm. The small absorptions noticed are no doubt due to the presence of a small quantity of metaphosphoric acid which, even at the temperature of  $400^{\circ}$ , distils over with the pentoxide. These experiments render it almost certain that the purified gases are not absorbed by purified phosphorus pentoxide.

Four experiments have been made with the purified gases since the publication of Herr Gutmann's paper, and they confirm the results which I have already published that the purified and dried gases do not produce white fumes or a decrease in volume when mixed, but that both these results follow the introduction of a little moisture. One cannot, of course, be sure what kind of phosphorus pentoxide Herr Gutmann used, but from the similarity of his results to that of the first experiment on ammonia described in this paper, it is likely that he was working with a material which contained metaphosphoric acid. Indeed, from the construction of his apparatus, it would appear that the different parts must have been sealed together after the introduction of the phosphorus pentoxide, and if this is so, moisture must of necessity have been introduced both from the blow-pipe flame, and from the air subsequently drawn through the apparatus to dry it. It may be pointed out, not only with reference to Herr Gutmann's experiments, but to those also of others who work in this field of research, that the mere passage of air, dried by sulphuric acid through a tube, is insufficient to dry it. It is, I think, always necessary to heat the tube to as high a point as possible during the passage of the dried air, in order to get rid of the moisture which adheres so tenaciously to glass. It may be mentioned here that Herr Gutmann has obtained an interesting result, which I had never observed, when the partially dried gases were mixed, namely, that a retardation took place in the velocity of the action, in one case as much as half an hour elapsed before the formation of ammonium chloride was complete.

With regard to the vapour density of dried ammonium chloride, I gave in 1894 a series of six determinations by Victor Meyer's method. They were

I.	II.	III.	IV.	V.	VI.	Mean.	Calculated for no dissociation.
28·8	29·5	26·3	28·6	26·8	26·8	27·8	26·75

The air expelled in these determinations was collected over freshly boiled mercury.

In view of the importance which has since been attached to the result that dried ammonium chloride does not dissociate, I may mention that, to avoid the possibility of any personal error being introduced, I asked Mr. F. R. L. Wilson, who was working in the Dulwich Laboratory, to make one complete determination. This he did, and obtained the result 26·8, which is a near approximation to the theoretical number. I mentioned in my paper that I had been unable to get the normal result by the use of Dumas' method for vapour densities. Since the paper was published, however, I have succeeded in doing this. By connecting the vapour density flask with a long phosphorus pentoxide tube which communicated with the

outer air by a long capillary tube, I obtained the result 28·8, which, under the circumstances, I regarded as satisfactory confirmation of the results obtained by the quicker method.

The vapour densities observed by Herr Gutmann after drying over phosphorus pentoxide for periods varying from 2 to 12 weeks are

	I.	II.	III.	IV.
Weeks .....	2	4	10	12
Vap. Den. ....	13·6	13·85	14·75	16·4

Here, again, our results differ very greatly, but I think the difference is easily explained. In the first two experiments, the air driven out of the apparatus was collected over water, and although there was a tube of phosphorus pentoxide interposed between the apparatus and the water, it appears to me impossible that a few molecules of water should not have passed back into the bulb. In the last two experiments, the air was collected over strong sulphuric acid. The same objection holds here, but of course not to the same extent, and it will be noticed that the results are slightly higher. One is inclined in doing such experiments as these to trust too much to the drying power of phosphorus pentoxide, and it is only after many failures that one realises how far one can go without putting the results in jeopardy.

I have great pleasure in acknowledging with gratitude the kindness of Mr. W. A. Shenstone in supplying me with a quantity of very highly purified phosphorus pentoxide when my own stock of it was very low. Only those who know the trouble of preparing substances so pure as this can appreciate such a piece of generosity.

DULWICH COLLEGE.

#### XLIV.—*Some Derivatives of Benzophenone.*

By FRANCIS EDWARD MATTHEWS, Ph.D.

IN continuation of work on the hexachlorides of benzene and its derivatives, it was found that, amongst other substances, benzophenone was capable of very readily yielding a chlorine additive compound. Unfortunately, however, this compound, a hexachloride, proved homogeneous, and therefore its investigation could not throw much fresh light on the cause of the isomerism existing among compounds of this class, although several substances of interest have been isolated in the course of the work.



*Preparation of Benzophenone Hexachloride.*

A strong solution of benzophenone in chloroform, in which it is exceedingly soluble, is covered with a layer of either water or dilute sodic hydroxide solution, and the mixture is saturated with chlorine. After saturation, the product is exposed either to bright light or to direct sunshine, when the colour of the chlorine rapidly disappears, and the mixture boils, evolving at the same time some hydrogen chloride produced by the action of the chlorine on the chloroform. After two or three saturations with chlorine, a considerable amount of a white, crystalline solid separates; this can be purified by pouring off the greater portion of the chloroform solution, filtering through coarse muslin, washing successively with fresh chloroform and absolute alcohol, and recrystallisation from benzene, acetic acid, or, better still, from xylene.

The purified recrystallised substance was analysed.

0.2258 gave  $\text{AgCl} = 0.4902$ .  $\text{Cl} = 53.7$ .

$\text{C}_6\text{H}_5\text{Cl}_6 \cdot \text{CO} \cdot \text{C}_6\text{H}_5$  requires  $\text{Cl} = 53.9$  per cent.

On treatment with alcoholic soda, it parts with 3 mols. of  $\text{HCl}$ . From 0.2369 of substance the chlorine removed was  $0.0625 = 26.4$  per cent. Theory for removal of  $\text{Cl}_2$  from  $\text{C}_6\text{H}_5\text{Cl}_6 \cdot \text{CO} \cdot \text{C}_6\text{H}_5 = 26.9$  per cent. The substance is therefore a hexachloride of benzophenone, and from other considerations it will be shown that the six atoms of chlorine are united with the same phenyl group. On fractionally crystallising a considerable quantity of the substance from acetic acid and xylene, no trace of a second modification could be found. An attempt was made to form a chlorine additive compound with the second  $\text{C}_6\text{H}_5$  group and thus obtain a dodecachloride, but without result. Benzophenone hexachloride is a colourless substance crystallising from acetic acid or xylene in beautiful transparent prisms or plates. When slowly heated, it sublimes unchanged, but when more rapidly heated it melts sharply at  $215^\circ$ . It is slightly soluble in all the ordinary organic solvents, especially on heating, but only very slightly so in cold chloroform, alcohol, benzene, or carbon bisulphide. On boiling with zinc dust in alcoholic solution, benzophenone is regenerated. The substance is not oxidised by chromic acid in boiling acetic acid solution even on long continued boiling, and potassic permanganate in acid solution is without action on it. As the compound is partly hydrolysed by sodic hydroxide (*vide infra*), an alcoholic solution was saturated with hydrogen chloride in the cold, but after three days no action had taken place. The substance is also unacted on by benzylic alcohol after digestion with the latter for 2 hours at its

boiling point. On heating with phosphorus pentachloride, no evidence of an action was obtained, and from the products nothing but the unaltered substance could be isolated.

On heating above its melting point, the hexachloride undergoes decomposition at about  $340^{\circ}$ , evolving torrents of hydrogen chloride accompanied by a considerable amount of benzoic chloride, identified by its boiling point and conversion into ethylic benzoate; on continuing the heating until the evolution of hydrogen chloride ceased, a heavy, yellow oil was obtained, which distilled without any further decomposition between  $315^{\circ}$  and a dull red heat. This oil was fractionated many times, but even after being left in a desiccator for three months, little or no solid separated from any of the fractions. The various fractions were then dissolved in cold acetone, and during the spontaneous evaporation of the latter, beautiful hexagonal prisms or plates were deposited from the fractions  $330\text{--}360^{\circ}$ , although the greater portion of the substance still remained liquid. After recrystallisation from acetone, the solid substance gave the following figures on analysis.

0.1170 gave  $\text{AgCl} = 0.1761$ .  $\text{Cl} = 37.2$ .

$\text{C}_6\text{H}_2\text{Cl}_3 \cdot \text{CO} \cdot \text{C}_6\text{H}_5$  requires  $\text{Cl} = 37.3$  per cent.

The oil varied in composition, and no concordant chlorine determinations were obtained.

Thus benzophenone hexachloride when heated gives hydrogen chloride, benzoic chloride, trichlorobenzophenone, and an oil of undetermined composition.

#### *Action of Alcoholic Soda on Benzophenone Hexachloride.*

As already shown, alcoholic soda removes 3 atoms of chlorine (3 mols. of  $\text{HCl}$ ) from the hexachloride. It was at first thought that the decomposition was represented by the equation



but on decomposing a larger quantity (28 grams) with excess of soda and precipitating with water, an oil was obtained which only partly solidified on standing. After remaining in a desiccator over soda-lime for a fortnight, the solid was removed from the oil by filtration, and the latter was fractionally distilled. It boiled constantly at  $208\text{--}210^{\circ}$  (uncorr.), and on analysis gave 58.8 per cent. of  $\text{Cl}$  ( $\text{C}_6\text{H}_3\text{Cl}_3 = 58.7$ ). Its nitro-derivative melted at  $57\text{--}58^{\circ}$ , showing that it was 1 : 2 : 4-trichlorobenzene. It therefore seemed probable that the benzophenone hexachloride was partly hydrolysed according to the equation  $\text{C}_6\text{H}_5\text{Cl}_6 \cdot \text{CO} \cdot \text{C}_6\text{H}_5 + \text{NaOH} = \text{C}_6\text{H}_5\text{Cl}_5 + \text{C}_6\text{H}_5 \cdot \text{COONa}$ , and that the benzene hexachloride formed was subsequently decomposed by the

soda, yielding  $C_6H_3Cl_3$ . This was found to be the case, as on concentrating the alkaline solution, and acidifying, a copious precipitate of benzoic acid was obtained, which, after two recrystallisations from hot water, melted at  $121-122^\circ$ .

The solid product of the reaction, purified by recrystallisation from acetone by spontaneous evaporation, formed large, colourless, hexagonal prisms.

0.2344 gave AgCl 0.3616. Cl = 38.1.

$C_6H_2Cl_3 \cdot CO \cdot C_6H_5$  requires Cl = 37.3 per cent.

The substance is, therefore, trichlorobenzophenone, and it agrees in all respects with the same substance prepared by the action of heat on the hexachloride. It is soluble in all the ordinary organic solvents, and crystallises well from most of them, especially acetone, in hexagonal prisms. It melts quite sharply at  $131^\circ$ .

An attempt was made to prepare a hexachloride from this substance, but without success.

The action of alcoholic soda on benzophenone hexachloride, therefore, results in the formation of trichlorobenzophenone, 1 : 2 : 4-trichlorobenzene, and benzoic acid.

#### *Nitration of Benzophenone Hexachloride.*

Benzophenone hexachloride dissolves readily in fuming nitric acid when heated, and on adding water a yellowish solid is precipitated. This was removed by filtration, washed until free from acid, and the funnel and its contents placed to dry in the water oven. The whole of the substance melted, and the small amount which was retained by the filter-paper solidified on cooling to an almost colourless, vitreous mass. Another portion was prepared, and after precipitation with water and thorough washing, was dissolved while still moist in acetone, in which it is very soluble; the yellow solution, on spontaneous evaporation, deposited crystals which became almost colourless on standing. These were recrystallised from alcohol, the yellow solution depositing yellow crystals; these melted at about  $120^\circ$ , with decomposition and evolution of a liquid (probably water of crystallisation). The yellow crystals were then dissolved in toluene, when the solution separated into two colourless layers; the upper layer, on being evaporated to dryness, left an almost colourless substance which, after two crystallisations from acetic acid, melted at  $159^\circ$ . On analysis, it gave the following result.

0.2872 gave AgCl 0.5646. Cl = 48.6.

$C_6H_5Cl_6 \cdot CO \cdot C_6H_4 \cdot NO_2$  requires Cl = 48.4 per cent.

The substance is, therefore, mononitrobenzophenone hexachloride.

It does not crystallise very well, but separates in very pale yellow needles from acetic acid or acetone; it is soluble in most organic solvents, and melts at  $159^{\circ}$ .

*Decomposition of Mononitrobenzophenone Hexachloride by Alkalis.*

A small quantity of the substance was dissolved in aqueous alcohol and decomposed by excess of sodic hydroxide; the amount of chlorine in solution was determined, and agreed well with the removal of 3 atoms of chlorine from 1 mol. of the substance.

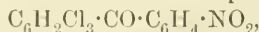
A much larger quantity was then decomposed in alcoholic solution, with rather more than the amount of soda (3 mols.) necessary for the removal of 3 atoms of chlorine; after boiling for an hour, although the liquid had become neutral, some of the nitro-derivative still remained undecomposed, and more sodic hydroxide was added, when the decomposition became complete. During the action, the solution became coloured, first reddish-yellow and then brown, probably from the formation of an azo-derivative. Some water was then added to the mixture, and the whole distilled on the water bath; the distillate was found to consist of a mixture of water, alcohol, and 1:2:4-trichlorobenzene, the last substance being identified by the melting point of its nitro-derivative ( $58^{\circ}$ ). During the distillation, a yellow solid separated, which was collected and purified by recrystallisation first from acetone and afterwards from glacial acetic acid, from which it separates in shuttle-shaped crystals. On further recrystallisation from acetone, it formed almost colourless, hexagonal plates, which gave the following result on analysis.

0.1265 gave  $\text{AgCl} = 0.1695$ .  $\text{Cl} = 33.1$

$\text{C}_6\text{H}_2\text{Cl}_3 \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2$  requires  $\text{Cl} = 32.2$  per cent.

The small amount of substance remaining precluded a second chlorine determination being made.

The substance is mononitrotrichlorobenzophenone,



and from the examination of the nitrobenzoic acid produced simultaneously, it is evident that the nitro-group is in the meta-position. It crystallises from acetone in hexagonal plates, melts sharply at  $143^{\circ}$  and is very soluble in the ordinary organic solvents. The filtrate from which the above substance had separated, after concentration, gave a copious red precipitate with hydrochloric acid; on dissolving this in water, when a small red residue was left, and twice recrystallising, a nearly colourless acid was obtained which melted at  $137\text{--}138^{\circ}$ . (Metanitrobenzoic acid melts at  $140^{\circ}$ .)

The barium salt prepared from this crystallised in shining needles



which contained  $4\text{H}_2\text{O}$ ; found  $\text{H}_2\text{O} = 13.2$ ; theory  $= 13.3$ . (The barium salts of the isomeric acids contain different amounts of water.) Also the saturated aqueous solution of the barium salt gave no precipitate with dilute nitric acid, which is a method of distinguishing the meta-acid from its isomerides.

The decomposition of metanitrobenzophenone hexachloride by alcoholic soda takes place chiefly according to the following equations,  $\text{C}_6\text{H}_5\text{Cl}_6 \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2 + 3\text{NaOH} = \text{C}_6\text{H}_2\text{Cl}_3 \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2 + 3\text{NaCl} + 3\text{H}_2\text{O}$ , and  $\text{C}_6\text{H}_5\text{Cl}_6 \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2 + 4\text{NaOH} = \text{C}_6\text{H}_3\text{Cl}_3 + \text{C}_6\text{H}_4 \cdot (\text{NO}_2) \cdot \text{COONa} + 3\text{NaCl} + 4\text{H}_2\text{O}$  although the decomposition is accompanied by the formation of a small amount of some azo-derivative.

*Action of Fuming Sulphuric Acid on Benzophenone Hexachloride.*

Benzophenone hexachloride dissolves readily in fuming sulphuric acid when heated with it to a temperature above its melting point. After allowing the solution to cool, adding water, and neutralising with barium carbonate, the aqueous solution contains a barium salt which crystallises in tufts of needles, and gave the following results on analysis.

1.1059 gave  $\text{H}_2\text{O} = 0.1203$  and  $\text{BaSO}_4 = 0.2080$ .  $\text{H}_2\text{O} = 10.87$ ;  $\text{Ba} = 11.06$ .  
 0.3981 „  $\text{H}_2\text{O} = 0.0437$  „  $\text{BaSO}_4 = 0.0755$ .  $\text{H}_2\text{O} = 11.00$ ;  $\text{Ba} = 11.15$ .  
 $(\text{C}_6\text{H}_5\text{Cl}_6 \cdot \text{CO} \cdot \text{C}_6\text{H}_4\text{SO}_3)_2\text{Ba} + 7\frac{1}{2}\text{H}_2\text{O}$  requires  $\text{H}_2\text{O} = 11.06$ ;  $\text{Ba} = 11.23$  per cent.

The substance is therefore the barium salt of a sulphonic acid of benzophenone hexachloride,  $\text{C}_6\text{H}_5\text{Cl}_6 \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_3\text{H}$ . The free acid was obtained as a non-crystalline, vitreous mass. It is readily acted on by sodic hydroxide, but as the products do not appear to crystallise well, they have not been further investigated.

All attempts to obtain a chlorine additive compound of acetophenone have been fruitless; the methyl group is so readily attacked by chlorine, that the chlorine cannot remain sufficiently long together with the  $\text{C}_6\text{H}_5$  group to produce an additive compound.

The most interesting points about the action of chlorine on benzophenone are that one phenyl group readily forms a hexachloride, but that the second one does not seem capable of doing so, and thus no dodecachloride can be obtained. This limit to the amount of chlorine capable of being taken up obtains likewise in the case of naphthalene, which in moist chloroform solution readily forms the tetrachloride, but does not yield any additive compounds containing a greater amount of chlorine than 4 atoms.

Another interesting point is the decomposition by alkalis of substances containing the group  $\text{C}_6\text{H}_5\text{Cl}_6 \cdot \text{CO}-$  (or  $-\text{CHCl} \cdot \text{CO}-$ ). Fittig has shown (*Ann.*, 1879, 195, 170) that substances which contain a



halogen atom and a carboxyl group joined to the same carbon atom are decomposed by sodium hydroxide in the cold, with removal of  $\text{CO}_2$ . This I have also found to be the case with the hexachlorides of benzoic acid, in some work which I hope will shortly be ready for publication, these hexachlorides, under the action of cold sodium hydroxide, being partly decomposed with the formation of sodic carbonate.

A more general statement is that substances containing the group  $-\text{CHCl}\cdot\text{CO}-$  undergo partial decomposition with cold sodium hydroxide, the  $\text{CO}$  group being removed.

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## XLV.—*The Chlorine Derivatives of Pyridine. Part I.*

By WILLIAM JAMES SELL, M.A., F.I.C., and FREDERICK WILLIAM DOOTSON, M.A.

### INTRODUCTION.

ALTHOUGH, according to our present views, there are nineteen possible chlorine substitution derivatives of pyridine, comparatively few of them have hitherto been prepared, and these have practically all been obtained by indirect methods. Moreover, when we come to consider the compounds whose constitution is established, this small number is still further restricted.

Briefly summarised, our knowledge of this class of compounds is limited to the following.

1.  $\alpha$ -Monochloropyridine, obtained from  $\alpha$ -hydroxypyridine (Pechmann and Baltzar, *Ber.*, 24, 3150).
2.  $\beta$ -Monochloropyridine, obtained from pyrroline (Ciamician and Dennstedt, *Gazzetta*, 11, 224, 300).
3.  $\gamma$ -Monochloropyridine, obtained from  $\gamma$ -oxyppyridine (Haitinger and Lieben, *Monats.*, 6, 315).
4. A dichloropyridine, melting point  $66-67^\circ$ , obtained from barium pyridinesulphonate, the position of the chlorine atoms being unknown (Königs and Geigy, *Ber.*, 1884, 17, 1833).
5. A trichloropyridine, melting point  $49-50^\circ$ , also obtained from the barium salt of pyridinesulphonic acid. One of the chlorine atoms is said to occupy the  $\alpha$ -position, the places of the others being unknown (Königs and Geigy, *loc. cit.*).
6. A trichloropyridine (?) (the note of interrogation is Seyffürth's), melting point  $64-65^\circ$ . This was obtained in too small a quantity to

be thoroughly examined. The orientation is unknown (Seyffürth, *J. pr. Chem.*, 1886, 2, 261).

To these may be added.

7. A tetrachloropyridine, in which the chlorine atoms occupy the  $\alpha\beta\alpha'\beta'$  positions, and

8. Pentachloropyridine, both obtained by the authors from citrazinic acid (*Trans.*, 1897, 71, 1068).\*

Keiser (*Am. Chem. J.*, 1886, 8, 308) has obtained a compound which he describes as a "hydrochlorate of di-chlor-pyridine" by the action of dry chlorine on dry pyridine, but, as will be shown later, this is not the hydrochloride of dichloropyridine, but a trichloropyridine.

In studying the action of phosphorus pentachloride on citrazinic acid, it was noticed that the hydrogen atoms of the nucleus were displaced by chlorine with the greatest ease by means of this reagent, even at atmospheric pressure. This suggested that an attempt should be made to chlorinate pyridine directly on similar lines. Königs and Geigy (*loc. cit.*) made some efforts to solve this problem, but their results do not appear to have been encouraging, and, so far as we are aware, nothing has been published.

The present communication deals exclusively with the interaction of phosphorus pentachloride and pyridine and some of the properties of the products thus obtained, the derivatives of these products being reserved for a future paper.

These products are:

1. Dichloropyridine melting at 87—88°
2. Trichloropyridine           ,,     49—50
3.                   ,,           ,,     71—72
4.                   ,,           ,,     67—68
5. Tetrachloropyridine       ,,     90—91
6.                   ,,           ,,     21—22
7.                   ,,           ,,     74—75
8. Pentachloropyridine       ,,     123—124
9. An oil, which forms a solid compound with mercuric chloride.
10. An oil which does not combine with mercuric chloride.

Thus the series above the trichlorinated derivatives is complete, and it is hoped that from (9) and (10) the remaining trichlorinated compounds, or some of them, may be isolated.

In these experiments, it was noticed that, although the higher chlorinated members of the series were abundant, the lower ones were

\* On the authority of Anschütz, a verbal statement was made by Kekulé to the German Chemical Society that he had obtained the last two compounds. The memoir on the subject was never written, but a private communication to Anschütz finds place in his edition of Richter's "*Organische Chemie*," 1896. No description beyond the melting points is given, only one of which approximates to anything described by us.

obtained in very small quantity ; nor was it found possible to prevent this, and all attempts to prepare the lower members, either by employing a lower temperature or a smaller proportion of phosphorus pentachloride, merely resulted in no action taking place at all in the former case, and, in the latter, in a smaller yield of practically the same products.

#### EXPERIMENTAL.

The first efforts in this chlorination were made by boiling pyridine with a saturated solution of phosphorus pentachloride in phosphorus oxychloride in a reflux apparatus, a method which had been so efficacious in the case of citrazinic acid, but it was found that even after boiling continuously for a fortnight, the original amount of pentachloride had diminished only very slightly, and on pouring the contents of the flask into cold water and distilling in a current of steam the yield of crude oil was very small.

After many attempts, the method finally adopted was to heat dry pyridine with 10 times its weight (approximately 4 mols.) of phosphorus pentachloride in sealed tubes to a temperature of  $210-220^{\circ}$  for from 15 to 20 hours, the tubes being frequently opened to allow the escape of hydrogen chloride. At this temperature, the pressure of gas in the tubes soon becomes very great, and loss from bursting tubes is almost unavoidable, whilst if a lower temperature is employed, the reaction is very slow and the operation tedious. The contents of the tubes were poured into cold water and distilled in a current of steam, when a brownish oil of a peculiar aromatic odour came over ; this was separated from the watery part of the distillate and allowed to stand overnight, when a small quantity of dense, hard crystals of pentachloropyridine separated. When nothing further came over with the steam, the contents of the flask were filtered from a small quantity of tarry matter, excess of lime was added, and the mixture again distilled in steam. The distillate was acidified with strong hydrochloric acid, concentrated, and excess of soda added, which caused the separation of a dark brown liquid ; this was removed, dried over soda, and distilled. The amount of material thus obtained was too small to investigate, but since it contained a fair proportion of chlorine, it seems probable that some of the lower chloropyridines were present.

The tarry residue, which is slightly soluble in alcohol and ether, was slowly heated to  $200^{\circ}$  under diminished pressure, when it frothed up violently, evidently decomposing, whilst practically nothing distilled over. It was not further examined.

*Isolation of the Products.*

The crude oil, filtered from the crystals of pentachloropyridine, was dissolved in methylated spirit, and a solution of mercuric chloride in alcohol added. On cooling, a copious crop of crystals separated; These were collected, using the pump, and more alcoholic mercuric chloride added, the operation being repeated until there was no further precipitate. The solution was then largely diluted with water, when that part of the oil which remained unacted on by the mercuric chloride was thrown down, together with a small quantity of the mercuric compound. This was drained by the aid of the filter pump, and the oil, separated from the dilute alcohol, was washed repeatedly with a saturated solution of sodium chloride to remove the last traces of mercuric chloride, and finally with distilled water. It was then dried in a vacuum over sulphuric acid, and distilled from an oil bath in a gentle stream of air at a pressure of 16—20 mm.

The mercuric compounds were recrystallised several times from alcohol, but, as a preliminary experiment had shown that it was hopeless to attempt a separation from such a complex mixture by recrystallisation alone, they were distilled in a current of steam from a saturated solution of sodium chloride, by which means the oil was liberated from the mercuric chloride. The same decomposition takes place on merely boiling with water, but is much hastened by the addition of sodium or potassium chloride. The last portions of the distillate, consisting of pentachloropyridine, solidified in the condenser. The pentachloropyridine, being very soluble in the crude oil, is thrown down in part on adding mercuric chloride, which removes a large portion of the principal solvent, and the pentachloropyridine cannot afterwards be easily separated from the mercuric compound by recrystallisation from alcohol, but, being less volatile than the other products, is chiefly found in the last portions of the steam distillate. It is therefore expedient to collect these separately.

The oil thus collected was separated from the watery part of the distillate, dried in a vacuum over sulphuric acid, and distilled from an oil bath in a gentle stream of air at a pressure of 16 mm. of mercury, the receiver being changed at intervals of 5°. The first portions began to distil over below 100°, and the distillation was practically complete at 140°; the portions thus collected were again fractionated separately as before, but were, however, far from being pure. Each was placed in a freezing mixture of ice and salt, when all became solid or semi-solid, and were in turn drained at the pump, the temperature meanwhile being allowed to rise slowly. This operation was repeated with each fraction as long as any solid residue was left on the filter

plate after it had attained the temperature of the laboratory. In this way, successive crops of crystals were obtained which were recrystallised from alcohol separately until the melting point of each was constant. They were then examined with the following results.

The crystals obtained from the fraction boiling below  $100^{\circ}$  at 16 mm. pressure were found to be a mixture of the two trichloropyridines melting at  $71-72^{\circ}$  and  $49-50^{\circ}$  respectively, the former being small in amount.

The fraction boiling between  $100^{\circ}$  and  $105^{\circ}$  yielded a trichloropyridine melting at  $49-50^{\circ}$

„ „ „  $105^{\circ}$  „  $110^{\circ}$  the same, in smaller amount.

„ „ „  $110^{\circ}$  „  $115^{\circ}$  the same, in very small amount.

„ „ „  $115^{\circ}$  „  $120^{\circ}$  A tetrachloropyridine. melting at  $21-22^{\circ}$ .

„ „ „  $120^{\circ}$  „  $125^{\circ}$  the same, together with some pentachloropyridine.

The fractions boiling above  $125^{\circ}$  all yielded pentachloropyridine; in each case there was an oily residue, which is under further examination.

The oil which had been freed from everything which forms a solid compound with mercuric chloride was in turn fractionated. This operation was repeated on each portion separately, and again on the fractions thus obtained, the receiver, as before, being changed in every case at intervals of  $5^{\circ}$ . The liquid began to distil at about  $100^{\circ}$ , under a pressure of 16—20 mm., and the operation was practically complete at  $140^{\circ}$ .

These fractions, like the former, were not pure products, the first two portions and the last partially solidifying on standing, and all depositing crystals on being placed in a mixture of ice and salt.

Since the number of compounds contained in each of these oils is obviously considerable, whilst the range of their boiling points is comparatively small, it is not surprising that such imperfect separation should be effected by these means, and it was evident that much larger quantities of the oil than had been prepared would be necessary before satisfactory separation could be obtained by the method of fractional distillation alone.

The crystals from each fraction were recrystallised from alcohol with the results stated below.

The fraction distilling below  $105^{\circ}$ , between  $105^{\circ}$  and  $110^{\circ}$ , and between  $110^{\circ}$  and  $115^{\circ}$  each yielded a dichloropyridine melting at  $87-88^{\circ}$ .

The fraction distilling at  $115-120^{\circ}$ , and  $120-125^{\circ}$ , a trichloropyridine melting at  $67-68^{\circ}$ .



The fraction distilling at 125—130°, a tetrachloropyridine melting at 90—91°.

The fraction distilling at 130—135°, a tetrachloropyridine melting at 74—75°, together with a little pentachloropyridine.

The fraction distilling above 135° yielded pentachloropyridine.

As in the former case, from each portion there was a residual oil which remained liquid at temperatures above 0°. These are being further examined.

#### DESCRIPTIVE.

*Dichloropyridine, melting at 87—88° (uncorr.).*—This was obtained in the manner described above from the first part of the distillate, which does not form an additive product with mercuric chloride. After several recrystallisations from 50 per cent. alcohol, it was obtained in rhomboidal plates of a glistening, satiny appearance, whose melting point was not changed by further recrystallisation. Analysis gave the following numbers.

I. 0.0888 gave 0.1308 CO<sub>2</sub> and 0.0154 H<sub>2</sub>O. C = 40.18; H = 1.92.

II. 0.1032 „ 0.1520 CO<sub>2</sub> „ 0.0180 H<sub>2</sub>O. C = 40.17; H = 1.93.

III. 0.0937 „ 8.0 c.c. of nitrogen at 14° and 763 mm. N = 10.06.

IV. 0.1303 „ 0.2550 AgCl. Cl = 48.44.

C<sub>5</sub>Cl<sub>2</sub>H<sub>3</sub>N requires C = 40.52; H = 2.02; Cl = 47.97; N = 9.46 per cent.

This dichloropyridine is very soluble in ether, benzene, light petroleum, chloroform, and hot alcohol; moderately so in cold alcohol, and insoluble in water. Strong mineral acids dissolve it readily on warming, and from these it is reprecipitated by diluting or neutralising. It does not form a double salt with platinic chloride.

*Trichloropyridine, melting at 49—50° (uncorr.).*—This was obtained from the crude compound with mercuric chloride described above, and was found in those parts of the distillate which came over between 100° and 120° (at 16 mm.). It crystallised from hot 50 per cent. alcohol in broad, flat needles, which melted constantly at 49—50°, and gave the following numbers on analysis.

I. 0.2787 gave 0.3333 CO<sub>2</sub> and 0.0271 H<sub>2</sub>O. C = 32.62; H = 1.08.

II. 0.2468 required 40.5 c.c. N/10AgNO<sub>3</sub>\*. Cl = 58.09.

C<sub>5</sub>H<sub>2</sub>Cl<sub>3</sub>N requires C = 32.87. H = 1.09; Cl = 58.35 per cent.

\* This chlorine determination, and some of the following ones, were made by fusing the substance with a mixture of equal weights of sodium and potassium carbonates, in the manner described by Schiff (*Ann.*, 1879, **195**, 293), subsequently dissolving in nitric acid, and estimating the soluble chlorides, with standard silver nitrate and ammonium thiocyanate (Volhard's method). If the fusion had been cautiously made, it was found that trustworthy results were obtained. The method has the advantage of being most expeditious, the whole operation requiring not more than half an hour.

This substance, which does not yield a compound with platonic chloride, is very soluble in ether, chloroform, acetone, benzene, and hot alcohol, moderately so in light petroleum and cold alcohol, and practically insoluble in water. A comparison of the properties, so far as they have been described, showed that it was identical with the trichloropyridine obtained by Königs and Geigy (*loc cit.*) by the action of phosphorus pentachloride on the barium salt of pyridinesulphonic acid.

In the present work, the yield of this product was greater than that of any of the others, with the exception of pentachloropyridine. It is plain, therefore, that the previous introduction of sulphonic groups into the pyridine nucleus is not necessary for its preparation.

*Trichloropyridine, melting at 71—72° (uncorr.).*—This was obtained from the compound with mercuric chloride, and was found in that part of the oily distillate which came over below 100° (at 16 mm.). It was found that when this compound was especially sought, it was more expedient to separate it from the other products of the reaction by distilling the first crop of the recrystallised mercuric compound, obtained as described above, separately, from a saturated solution of sodium chloride, the receiver being changed as soon as the distillate no longer solidified on cooling. Recrystallised from 50 per cent. alcohol, this compound was obtained in silky needles which became opaque on exposure to the air. These needles melted constantly at 71—72°, and gave the following numbers on analysis.

I. 0.1243 gave 0.1515  $\text{CO}_2$  and 0.0120  $\text{H}_2\text{O}$ .  $\text{C} = 33.24$ ;  $\text{H} = 1.08$ .

II. 0.1123 „ 0.2660  $\text{AgCl}$ .  $\text{Cl} = 58.61$ .

$\text{C}_5\text{Cl}_3\text{H}_2\text{N}$  requires  $\text{C} = 32.93$ ;  $\text{H} = 1.09$ ;  $\text{Cl} = 58.35$  per cent.

This trichloropyridine is very soluble in chloroform, ether, benzene, acetone, light petroleum, and hot alcohol, and more sparingly in cold alcohol; it is dissolved to a slight extent by boiling water, from which it crystallises on cooling in long, silky needles. Strong hydrochloric, nitric, and sulphuric acids dissolve it readily, and from these it is reprecipitated on diluting or neutralising.

If to its alcoholic solution an alcoholic solution of mercuric chloride be added, the double compound is obtained in long, fine needles, which are insoluble in water and only very sparingly soluble in cold alcohol, although hot alcohol and ether dissolve them readily. These needles melt at 168—170° (uncorr.), and from the following mercury and chlorine determinations have the composition expressed by the formula  $(\text{C}_5\text{H}_2\text{Cl}_3\text{N})_2, \text{HgCl}_2$ .

I. 0.4020 gave 0.1247  $\text{Hg}$  and 0.7220  $\text{AgCl}$ .  $\text{Hg} = 31.02$ ;  $\text{Cl} = 44.46$ . Calculated for the above formula,  $\text{Hg} = 31.49$ ;  $\text{Cl} = 44.46$  per cent.

Treated with cadmium chloride in a similar way, a compound is ob-

tained which crystallises in rosettes of short, thick needles, which are insoluble in water and nearly so in cold alcohol.

If to the alcoholic solution of this trichloropyridine a solution of chloroplatinic acid be added, a crystalline, yellow precipitate is obtained on long standing in the cold, or immediately on boiling; this, when dried in the air, contains no water of crystallisation, and, from the results of a platinum determination, seems to have the composition represented by the formula  $(C_5Cl_3H_2N)_2PtCl_4$ , as the following numbers show.

I. 0.2340 gave 0.0658 Pt.  $Pt = 28.12$ .

Calculated for the above formula,  $Pt = 27.66$  per cent., whilst the formula  $(C_5Cl_3H_2N)_2H_2PtCl_6$  requires  $Pt = 25.13$  per cent.

This compound with platinic chloride is practically insoluble in water and alcohol. From it, the base is most conveniently re-obtained by subjecting it to a gentle heat in a stream of dry hydrogen. It was not found possible to recover it by the action of aqueous hydrogen sulphide.

*Trichloropyridine melting at  $67-68^\circ$  (uncorr.).*—This was obtained from that portion of the crude oil which did not form a compound with mercuric chloride, and was frozen out from the fractions boiling between  $115^\circ$  and  $125^\circ$  (at 16—20 mm.). It is very soluble in hot alcohol, from which it crystallises on cooling in long, somewhat flattened needles; it is fairly soluble in cold alcohol, and, indeed, shows the same general solubility in the ordinary organic solvents as the previously described trichloropyridines. Although readily soluble in hot, strong mineral acids, it crystallises out for the greater part, on cooling, and does not appear to be quite so basic as the others. It is readily distinguished and separated from them by its forming no additive products with either cadmium chloride, mercuric chloride, or platinic chloride.

I. 0.2535 gave 0.3037  $CO_2$  and 0.0260  $H_2O$ .  $C = 32.67$ ;  $H = 1.14$

II. 0.1830 required 30.2 c.c. of  $N/10 AgNO_3$ .  $Cl = 58.41$ .

$C_5Cl_3H_2N$  requires  $C = 32.87$ ;  $H = 1.09$ ;  $Cl = 58.35$  per cent.

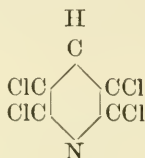
*Tetrachloropyridine, melting at  $90-91^\circ$  (uncorr.).*—The fraction of the oily distillate boiling between  $125^\circ$  and  $130^\circ$  (at 16—20 mm.), obtained from that portion of the original oil which forms no compound with mercuric chloride, on being recrystallised several times from methylated spirit, had a constant melting point,  $90-91^\circ$ , and gave the following numbers on analysis.

I. 0.1126 gave 0.0058  $H_2O$  and 0.1144  $CO_2$ .  $C = 27.70$ ;  $H = 0.57$ .

II. 0.1000 required 18.45 c.c.  $N/10 AgNO_3$ ;  $Cl = 65.26$ .

$C_5Cl_4HN$ , requires  $C = 27.66$ ;  $H = 0.46$ ;  $Cl = 65.44$  per cent.

Whilst closely resembling the trichloropyridines in general solubility, it is dissolved to a less extent by organic solvents, and is quite insoluble in water. In crystalline form and general properties, it agrees entirely with the tetrachloropyridine obtained by the authors from citrazinic acid (Trans., 1897, 71, 1031), and is obviously identical with it. Hence its structure must be represented by the formula



*Tetrachloropyridine, melting at 21—22° (uncorr.).*—This was obtained from the compound with mercuric chloride, and was found in that portion of the distillate boiling between 120° and 125° (at 16 mm.). It separates from this oily distillate, on standing in a cold place, in transparent, massive crystals, which readily melt at the temperature of the hand. From alcoholic solution, at temperatures below 20°, it crystallises in needles, which, if the alcohol be allowed to evaporate slowly, grow to a large size. It is very soluble in ether, chloroform, benzene, and the usual organic solvents, very sparingly so in strong hydrochloric acid, and insoluble in water. It does not yield a compound with cadmium chloride or chloroplatinic acid, although it very readily unites with mercuric chloride, forming an easily crystallisable and well-defined salt. The following numbers were obtained on analysis.

I. 0.1387 gave 0.1387 CO<sub>2</sub> and 0.0043 H<sub>2</sub>O. C = 27.27; H = 0.35.

II. 0.1799 required 33.2 c.c. N/10 AgNO<sub>3</sub>; Cl = 65.28.

C<sub>5</sub>Cl<sub>4</sub>HN requires C = 27.66; H = 0.46; Cl = 65.44 per cent.

*Tetrachloropyridine, melting at 74—75° (uncorr.).*—This was contained in the second of the oils described above, and was frozen out from the fraction boiling between 130° and 135° (at 16—20 mm.). The yield was very small. On recrystallising from alcohol several times, the substance melted sharply at 74—75°, and this melting point was not changed by subsequent recrystallisation. After three such purifications, it gave the following numbers on analysis.

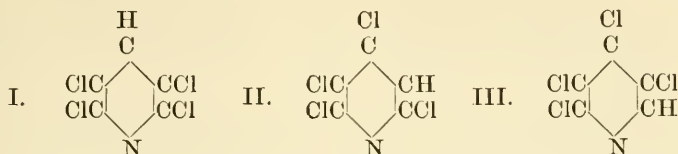
I. 0.1537 gave 0.1580 CO<sub>2</sub> and 0.0050 H<sub>2</sub>O. C = 28.04; H = 0.38.

II. 0.1070 required 19.7 c.c. N/10 AgNO<sub>3</sub>. Cl = 65.12.

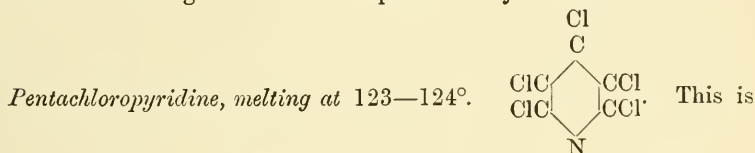
C<sub>5</sub>Cl<sub>4</sub>HN requires C = 27.66; H = 0.46; Cl = 65.44 per cent.

It crystallises from 50 per cent. alcohol in thin, elongated, rectangular plates. It is very soluble in ether and the usual organic solvents, but insoluble in water and acids. It forms no additive compound with mercuric chloride, cadmium chloride, or chloroplatinic acid.

Of the three possible tetrachloropyridines, it has been shown above that the compound melting at  $90-91^{\circ}$  has the constitution represented by the formula I.



And the remaining two must, therefore, be represented by the formulæ II and III. As to which of the two tetrachloropyridines described above these formulæ respectively belong is an open question, but, so far as our present knowledge extends, it is probable that the compound melting at  $74-75^{\circ}$  has the constitution represented by formula II, whilst that melting at  $21-22^{\circ}$  is represented by formula III.



by far the most abundant and most easily isolated of the products of the action of phosphorus pentachloride on pyridine; a portion of it separates from the crude oil on standing, and the remainder is found in the last fractions of both distillates described above. Although volatile in steam, it is much less so than any of the other products of the reaction, and, consequently, in the distillations with steam, was always found chiefly in the last portions which came over.

From boiling alcohol, it crystallises in cubes, or modifications of cubes, frequently in skeleton forms resembling ammonium chloride. It is dissolved by the same organic solvents as are the tetrachloropyridines, but to a much smaller extent. The following numbers were obtained on analysis.

- I. 0.1460 gave 0.1275  $\text{CO}_2$  and 0.0015  $\text{H}_2\text{O}$ .  $\text{C} = 23.81$ ;  $\text{H} = 0.10$ .  
 II. 0.2450 „ 0.2100  $\text{CO}_2$  „ 0.0005  $\text{H}_2\text{O}$ .  $\text{C} = 23.42$ ;  $\text{H} = 0.02$ .  
 III. 0.2307 „ 10.7 c.c. moist nitrogen at  $16.5^{\circ}$  and 766 mm.  $\text{N} = 5.44$ .  
 IV. 0.1220 „ 0.3470  $\text{AgCl}$ .  $\text{Cl} = 70.40$ .

$\text{C}_5\text{Cl}_5\text{N}$  requires  $\text{C} = 23.90$ ;  $\text{Cl} = 70.51$ ;  $\text{N} = 5.58$  per cent.

Pentachloropyridine thus prepared coincides in every way with that obtained by the authors from citrazinic acid (*loc. cit.*).

In conclusion, the authors desire to express their thanks to Mr. H. Jackson, B.A., B.Sc., for his assistance in the analyses.



XLVI.—*Note on the Action of Chlorine on Pyridine.*

By WILLIAM JAMES SELL, M.A., F.I.C., and FREDERICK WILLIAM DOOTSON, M.A.

IN the preceding communication, the authors described a trichloropyridine fusing between  $71^{\circ}$  and  $72^{\circ}$ . The coincidence between this melting point and that assigned by Keiser (*Am. Chem. J.*, 1886, 8, 310) to a compound which he describes as the hydrochloride of dichloropyridine,\* together with the great similarity in properties of the two compounds, suggested that they might be identical. With the object of investigating this point, Keiser's work was in part repeated.

At the outset, it was not intended to prosecute the search in this direction further than the isolation of sufficient of the substituted product for comparison, since the results which had been obtained by Keiser did not seem to hold out much prospect that the method would prove a serviceable one for the object with which the authors were concerned, namely, the preparation of the chloropyridines. However, in the course of the work, conclusions were arrived at differing so materially from those of Keiser, that the action of dry chlorine on dry pyridine was studied at somewhat greater length.

The general plan of Keiser's investigation was to pass dry chlorine into dry pyridine, and separate the products by fractional distillation. The substances thus obtained were (1) the excess of pyridine used, coming over at  $116^{\circ}$ ; (2) the so-called hydrochloride of dichloropyridine, partly mixed with pyridine, and partly condensing in the neck of the retort, distilling at  $130^{\circ}$ ; (3) a substance distilling at  $218$ — $219^{\circ}$  and condensing to a waxy solid, regarded by Keiser as an additive compound, having the formula  $C_5H_5NCl$ ; (4) a tarry residue of unknown composition.

No mention is made of the temperature at which the chlorination was effected, or of the relative amounts of material used, although, from the results obtained, the chlorine could not have been in excess.

In repeating the work, therefore, experiments were made at temperatures varying from  $0^{\circ}$  to the boiling point of pyridine, whilst the stream of chlorine was sometimes continued until hydrogen chloride was freely evolved. It was not found that the yield of the substance sought was materially affected by this variation of treat-

\* The authors desire to point out that the melting point of this "hydrochlorate of dichloropyridine" is erroneously given in Muir and Morley's edition of Watts' dictionary of chemistry as the melting point of dichloropyridine itself, which latter, as is stated in the memoir, was never obtained.

ment, although the amount of residual tarry matter increased with rise of temperature.

In all cases where heat was employed, a light, feathery sublimate settled in the colder parts of the flask, which was in most cases removed before proceeding to the separation of the other products. This compound has a faint odour resembling that of bleaching powder and is partly soluble in water. Its hot alcoholic solution deposits an oil on cooling, and, later, needle-like crystals appear; its aqueous solution gives a heavy, white precipitate with silver nitrate, insoluble in nitric acid. In general properties and appearance, it recalls the compound obtained by Anderson (*Trans. Roy. Soc. Edin.*, 1857). It was not further examined, but the authors hope shortly to have an opportunity of more fully investigating this substance.

In some cases, the separation of the remaining products was effected as in Keiser's experiments, but in consequence of the violent frothing of the contents of the flask as the temperature rose, this method was abandoned in favour of distillation in a current of steam, by which means separation was more easily obtained. The oil which separated from the first portions of the steam distillate solidified on cooling, and when drained by the aid of the filter pump and recrystallised several times from alcohol, was obtained in long, colourless needles melting between  $71^{\circ}$  and  $72^{\circ}$ , and identical with the product obtained by fractional distillation. Later portions of the distillate contained an oil which did not solidify on cooling, and, in appearance and properties, resembled the oil obtained by the action of phosphorus pentachloride on pyridine (p. 434), which has been shown to be a mixture of chlorine substitution products of pyridine, for the greater part at least. The yield of this oil was, however, too small to render the method an advantageous one for its preparation.

The amount of black tarry mass remaining in the flask after the steam distillation was complete was considerable; it was carefully dried, and an attempt made to distil it under diminished pressure, but although the temperature was cautiously and slowly raised to  $250^{\circ}$  (15 mm.), practically nothing distilled over, whilst the contents of the flask frothed violently, giving off pungent smelling gases. It was not further examined.

That the crystalline compound melting at  $72^{\circ}$  is not the hydrochloride of a base, is shown by the fact that its solution in alcohol or strong nitric acid gives no precipitate with silver nitrate.

The only evidence adduced by Keiser that it has the constitution expressed by the formula  $C_5H_3Cl_2N.HCl$ , lies in a chlorine determination, and an estimation of the residual platinum obtained by heating the double compound of this substance with platinic chloride. No carbon and hydrogen determination was made. It is plain that

the hydrogen determination is crucial, and analyses made on the compound separated by fractional distillation in the manner described by Keiser, and which melted between  $71^{\circ}$  and  $72^{\circ}$ , give the following numbers.

- I. 0.1775 gave 0.2132  $\text{CO}_2$  and 0.0166  $\text{H}_2\text{O}$ .  
 II. 0.2299 „ 0.2776  $\text{CO}_2$  „ 0.0250  $\text{H}_2\text{O}$ .  
 III. 0.1343 „ 0.3131  $\text{AgCl}$ .  
 IV. 0.2051 „ 13.6 c.c. nitrogen at  $14^{\circ}$  and 767 mm.

Calculated for	Calculated for	Found.			
$\text{C}_5\text{H}_3\text{Cl}_2\text{N} \cdot \text{HCl}$ .	$\text{C}_5\text{Cl}_3\text{H}_2\text{N}$ .	I.	II.	III.	IV.
C = 32.57	32.87	32.75	32.93	—	—
H = 2.17	1.09	1.04	1.20	—	—
Cl = 57.65	58.35	—	—	57.68	—
N = 7.60	7.69	—	—	—	7.95

The double compound, which crystallises out from the alcoholic solution of this substance on adding platinic chloride, gave 27.60 per cent. of platinum (Keiser). This agrees very nearly with the corresponding salt of trichloropyridine described by the authors, who found 28.12 per cent. of platinum.

This double compound, therefore, should have the constitution expressed by the formula  $(\text{C}_5\text{H}_2\text{Cl}_3\text{N})_2\text{PtCl}_4$  (calculated, Pt = 27.66 per cent.), analogous to that obtained from pyridine by long continued boiling with platinic chloride. The formula  $(\text{C}_5\text{Cl}_3\text{H}_2\text{N})_2\text{H}_2\text{PtCl}_6$  requires Pt = 25.13 per cent.

If an alcoholic solution of mercuric chloride is added to the alcoholic solution of the chloropyridine, crystals are obtained which, after purification, melt without decomposition at  $168$ — $170^{\circ}$ , and are identical with the compound shown by the authors (*loc. cit.*) to have the composition expressed by the formula  $(\text{C}_5\text{Cl}_3\text{H}_2\text{N})_2\text{HgCl}_2$ .

There can, therefore, be no doubt that the compound obtained by Keiser is not a hydrochloride of dichloropyridine, but a trichloropyridine identical with that obtained by the action of phosphorus pentachloride on pyridine.

It should here be further pointed out that the reasons adduced for assigning the formula  $\text{C}_5\text{H}_5\text{NCl}$  to the third fraction of the distillate, which constitutes the "yellow waxy solid," boiling between  $218$ — $219^{\circ}$ , are inadequate. This product agrees, so far as its properties have been described in Keiser's memoir, with hydrochloride of pyridine. On searching the literature on the subject, no record could be found of the boiling point of hydrochloride of pyridine, but an experiment showed that it distilled unchanged at  $218$ — $219^{\circ}$  (uncorr.).

Since, in Keiser's experiments, unchanged pyridine was recovered by distillation and a substitution of chlorine for hydrogen had

undoubtedly taken place, hydrochloride of pyridine must have been present; on the other hand, it is extremely unlikely that an additive product, having the constitution given, would distil unchanged at exactly the same temperature as hydrochloride of pyridine.

Further, by an error in the calculation of the analysis quoted in support of this contention, Keiser gives the percentage of hydrogen, which ought to be 5.05 per cent., as 4.68 per cent. With this correction, the analyses obtained agree more nearly with the numbers required for hydrochloride of pyridine than with those required by the formula  $C_5H_5NCl$ , as is seen below.

Calculated for $C_5H_5N \cdot Cl$ .	Calculated for $C_5H_5N \cdot HCl$ .	Found (Keiser).
C = 52.39	51.94	52.00
H = 4.37	5.20	5.05* (4.68)
Cl = 30.96	30.70	30.89

The double compound obtained by the addition of platonic chloride to an aqueous solution of this substance is admittedly pyridine platinum chloride.

The conclusions arrived at therefore are.

1. There is, without doubt, an additive product of pyridine and chlorine formed, as to the constitution of which there is, as yet, no conclusive evidence.
2. The so-called hydrochloride of dichloropyridine is a trichloropyridine.
3. Other chloropyridines are formed in small amount.
4. The compound described as an additive product of chlorine and pyridine, to which the formula  $C_5H_5NCl$  has been assigned, is really hydrochloride of pyridine.

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## XLVII.—*A Possible Basis of Generalisation of Intramolecular Changes in Organic Compounds.*

By ARTHUR LAPWORTH, D.Sc.

THE question of the manner in which substitution, isomeric change, &c., are interrelated has for a long time engaged the attention of many chemists. Up to the present, however, no consistent generalisation has been made.

Perhaps the only attempt to solve any considerable portion of the

\* 0.2691 gave 0.5131  $CO_2$  and 0.1223  $H_2O$ .

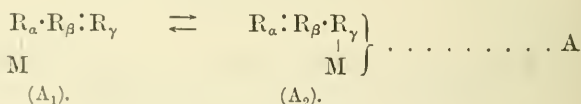
problem was that made by Armstrong (Trans., 1887, 51, 258) in a paper dealing with the theory of substitution and isomeric change in benzenoid compounds. In this paper, attention was drawn to the fact that two theories may be held with regard to the manner in which substitution is effected. The first was that due to Williamson ("Theory of Etherification," 1851), and the second, that brought forward, probably for the first time, by Kekulé (*Lehrbuch*, 1867).

In Williamson's paper, the suggestion was made that the first stage of substitution consists in the action between dissociated portions of the interacting compounds, whilst in Kekulé's paper it is assumed that initial combination or association is to be regarded as responsible for the production of the substitution product.

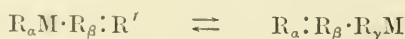
It is probable, of course, as Armstrong suggests, that both views are correct, the first phenomenon occurring in some cases, and the second in others. Thus initial dissociation must be assumed to occur when, for example, a saturated hydrocarbon is attacked by chlorine, and that a preliminary addition of the "dissociated" portions of a substituting agent, such as nitric acid, to the nucleus of benzene, takes place when the latter is nitrated. The exact manner in which preliminary dissociation of a reacting compound takes place may for the present be regarded as an open question.

In the present paper, the author having taken as starting point the hypotheses of Williamson and Kekulé, hopes to demonstrate that it is possible to refer the majority of reactions and changes in organic chemistry to necessary variations of one, or at most two, simple laws, which laws find their most general forms in the relationship between, for example, the two forms of "tautomeric" and "desmotropic" substances.

The relationship of these forms (where alteration of affinity or valency is excluded) may be represented by means of the following general scheme, which will here, for convenience, be referred to as form A.



or as usual, for brevity



where  $R_{\alpha}$ ,  $R_{\beta}$ ,  $R_{\gamma}$  are atoms united to one another in the manner shown, and M is a "univalent" atom or radicle, *labile* under the conditions in question; the sign  $\rightleftharpoons$  represents, as usual, a reversible change.

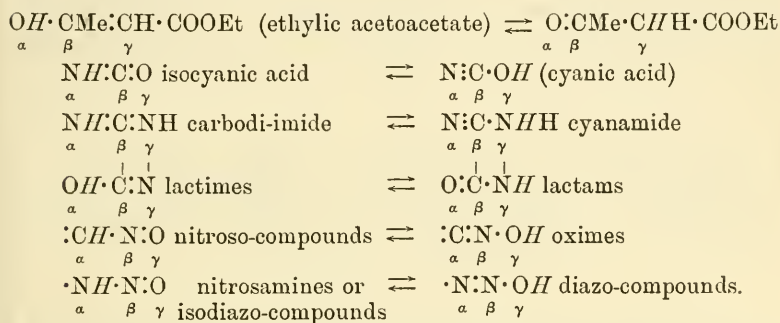
The labile group M, it will be observed, moves from the  $\alpha$ -atom to



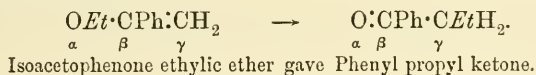
attach itself to the  $\gamma$ -atom, the suitable rearrangement of the linkings taking place between the three fixed atoms  $R_\alpha$ ,  $R_\beta$ , and  $R_\gamma$ .

In desmotropic substances, both forms corresponding to  $A_1$  and  $A_2$  are known. Tautomerism, as is now generally recognised, may be taken as the expression of the instability of one form, as each form may usually be obtained in one or more of its more stable derivatives.

The following examples of the above type of change will serve to make clear its applicability.

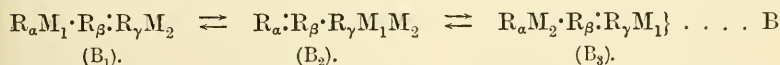


The following is a most interesting example noticed by Claisen (*Ber.*, 1896, 29, 2931).



It will be seen that in the special form A,  $R_\alpha$  and  $R_\gamma$  may be O, N, or C, and  $R_\beta$  may be N or C; obviously, oxygen is excluded from occupying the position  $R_\beta$ , as in ( $A_1$ ) and ( $A_2$ ) this must be at least a triad element. As will be shown later, other groups may functionate in place of C, N, or O.

If now, labile groups  $M_1$  and  $M_2$  are attached to  $R_\alpha$  and  $R_\gamma$ , as in ( $B_1$ ), we should expect by a logical extension of A to observe on occasion a change such as

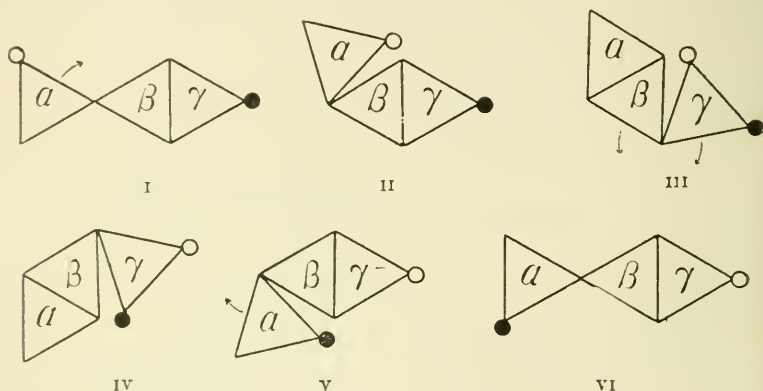


that is, in a grouping such as ( $B_1$ ), labile groups attached to  $R_\alpha$  and  $R_\gamma$  might change places without any final alteration of the original disposition of the single and ethylenic linkings.

A "mechanical" explanation of the forms A and B is not hard to find, as will be seen by a consideration of the following diagram, where carbon atoms in the form of tetrahedra are shown, for convenience, in projection as triangles, as in A and B we are only concerned with triad or diad atoms or radicles  $R_\alpha$ ,  $R_\beta$ , and  $R_\gamma$ . The

single linkings are, as usual, supposed to exist at the corners, and the ethylenic, or double linking, is represented in the conventional manner, as union of the edges of two tetrahedra.

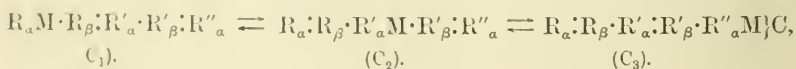
FIG. 1.



As will be clearly seen by means of the diagram, the formation of an ethylenic union between the atoms  $a$  and  $\beta$  brings one of the labile groups, which are represented by the small black and white circles, into close proximity with the point of attraction of the atom  $\gamma$ , and, as the latter is released, its union with the labile group is a most natural result.

It is not necessary, of course, to imagine that the group  $M$  ever actually becomes free, but rather that it is always under the influence of the attraction of  $R_a$  or  $R_\gamma$ , and possibly, at some instant, of both simultaneously; thus the lability of the molecule may be imagined to depend on a species of "dissociation." By the latter word, the author wishes to express more especially the idea that the combination of two portions of a molecule is of so little intimacy that, under the influence of disturbing attractions, the union between the dissociated portions may be readily overcome.

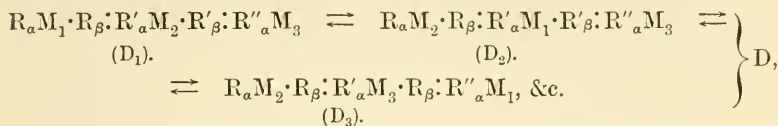
Now, should the grouping  $A_1$  or  $B_1$  be merely the commencement of a chain of alternately singly and doubly linked atoms as in  $C_1$  and  $D_1$ , it would be most naturally expected that successive changes, exactly similar to  $A$  and  $B$  respectively, would go on under favourable conditions, as represented by forms  $C$  and  $D$ ,  $R'_a$ ,  $R''_a$ , &c., functioning in turn as  $R_\gamma$  does in the forms  $A$  and  $B$ .



that is, a labile group might move along a chain of alternately singly

and doubly bound atoms, *the ethylenic and single linkings changing places in the path of the labile group.*

Again, by B, we have



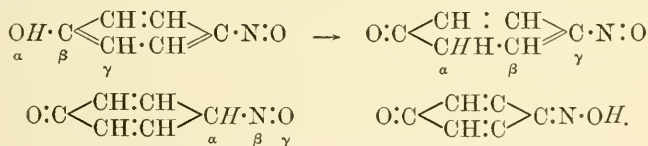
that is, in a chain composed of alternately singly and doubly linked atoms, labile groups attached in  $\gamma$ -positions (once, twice, or even more removed) with regard to one another, might change places without any final alteration of the original disposition of linkings in the chain.

For examples of changes corresponding with types C and D, reference may be made to benzenoid derivatives. If benzene and its derivatives be represented by Kekulé's formula, it is at once seen that the alternate single and double linkings are here existent, thus

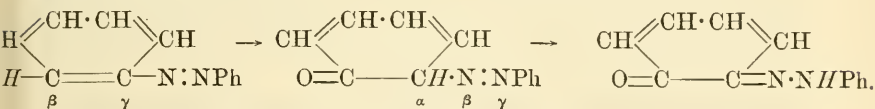


and, as it is probable that all benzenoid derivatives act, on occasion, as if they had Kekulé's formula, no exception can be taken to this mode of representing them.

A few examples of isomeric change, probably referable to forms C and D, may conveniently be taken here. Thus, on making nitroso-phenol, the product obtained is quinone-oxime, and the following scheme represents their tautomerism most perfectly. (In this, and in all the following examples, the labile group is in italics for the sake of clearness.)



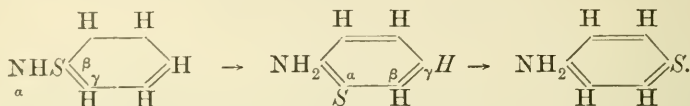
In like manner, orthohydroxyazobenzene is tautomeric with orthophenylquinone hydrazone.



As examples of type D, the changes observed in many sulphonic acids of the benzenoid series may be quoted; namely, those which undergo isomeric change in absence of any considerable quantity of free sulphuric acid (in which case hydrolysis and re-sulphonation and

like changes are doubtless impossible or highly improbable). In these cases the sulphonic groups wander into  $\gamma$ -positions (possibly once or twice removed) with regard to their original ones.

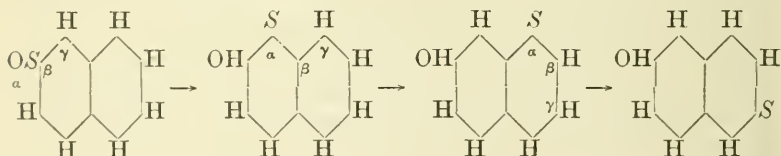
1st. The change of phenylsulphamic acid, successively, to ortho- and para-anilinesulphonic acids (here  $S = SO_3H$ ).



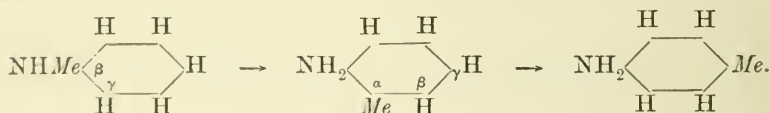
As the barium salt of phenylsulphamic acid, when heated, changes into that of paranilinesulphonic acid, the occurrence of hydrolysis and resulphonation is in this case entirely excluded.

An even more striking instance of this type of isomeric change is seen in the changes of  $\beta$ -naphtholsulphonic acids. These (by analogy with phenol), probably from  $\beta$ -naphthyl sulphate as initial compound, go through three changes, which, as the author has shown (Proceedings, 1895, 49) by the investigation of the corresponding compounds of  $\beta$ -ethoxynaphthalene, may be regarded as successive.

In the following scheme, as in many of the succeeding cases, the nuclei are represented by means of the ordinary skeleton formula, the double linkings being left out.



The change of methylaniline into toluidine is doubtless of a similar kind.



It is probable, however, as in many similar cases, that the molecule does not revert to the benzenoid condition until the labile group is in the para-position. In this event, an intermediate compound would

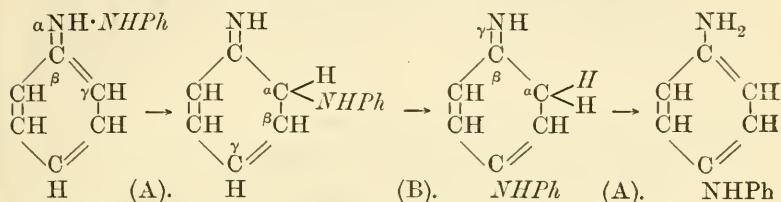
be produced, namely,  $\text{NH}:\text{C} \begin{array}{c} \text{H} \quad \text{H} \\ \diagdown \quad \diagup \\ \text{C}=\text{C} \\ \diagup \quad \diagdown \\ \text{C} \cdot \text{CH} \end{array} \text{CH}$ , which would finally re-

adjust itself, the methyl group being the first to move.

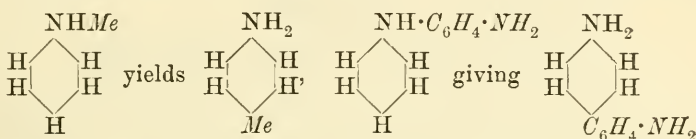
To this type also, may be referred the formation of parachlor-

acetanilide from phenylchloracetamide (Benda, *Ber.*, 1886, 19, 2273), &c., and the more complicated cases of ortho- and para-amidoazobenzenes from diazoamidobenzenes, as well as that of benzidines from hydrazobenzenes.

The latter may be represented for simplicity thus



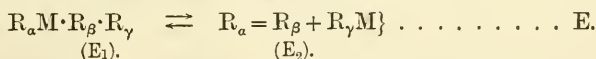
The changes being in each case labelled according to their form. The last pictured compound would furnish benzidine in the same manner as methylaniline yields toluidine.



The two changes thus represented, however, must probably be regarded as simultaneous and not successive, and it is not suggested that paramidodiphenylamine is actually an intermediate compound, although the latter would probably yield benzidine under suitable treatment.

Before proceeding with the discussion of isomeric change in the benzene series, it will be advantageous if, at this stage, some further consequences of change A be pointed out.

If, in a compound containing the group  $E_1$ , the union between  $R_2$  and  $R_3$  be a readily severable one, a change similar to that of  $A_1$  to  $A_2$  will produce that of  $E_1$  to  $E_2$ , that is to say, separation of the molecule into 2 parts between  $R_\beta$  and  $R_\gamma$  will result.

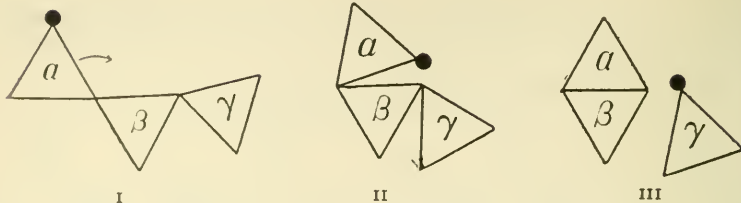


This formula may for convenience be termed the "scission formula."

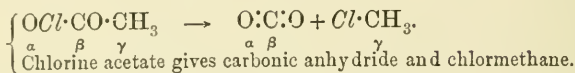
Of this type of change, examples are, of course, without number, and its "mechanical" explanation is readily understood by a glance at Fig. 2, where it is seen that the changes are exactly comparable with those of A and B as represented in Fig. 1.



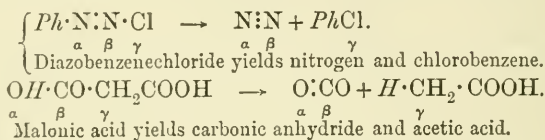
FIG. 2.



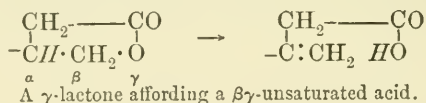
The following examples may be quoted.



(Schutzenberger. *Leçons professées en 1868 and 1869 devant la Société Chimique de Paris*).



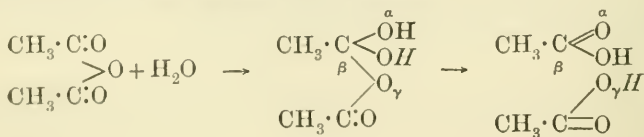
Amongst unsaturated acids, many interesting cases are known. (Compare Fittig, *Ber.*, 1894, 27, 2658). Thus, as an example of ring scission on the basis of type E.



We are now in a position to derive conclusions of considerable value from the use of the foregoing considerations, more especially if we combine with Kekulé's hypothesis that addition as a rule precedes substitution, the idea (first brought forward for a special case by Armstrong) that isomeric change is, in many cases, an intermediate phenomenon in the formation of the final products.

The following cases of hydrolysis may serve to make clear the manner in which the theoretical methods of investigation brought forward in the present paper may be employed. The type of change is in each case labelled with the appropriate letter for convenience in reference.

#### 1. Hydrolysis of acetic anhydride by alkalis.

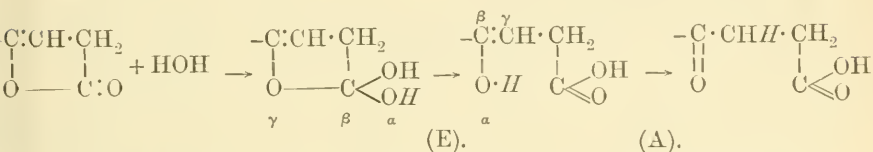


Probably, however, the labile group is the metallic ion introduced. In any case, the final product is, of course, two molecules of acetate.

The enormous difference in stability between acidyl and alkyl oxides receives in this manner an excellent explanation, as in the latter, additive compounds of the above type are not formed, and the hydrolysis must be preceded by the dissociation of the saturated alkyl oxide.

2. The hydrolysis of ethylic acetoacetates, &c., by alkali in several different ways may be represented in an exactly similar manner.

3. The interesting change of unsaturated lactones into ketonic acids may be written in this manner.

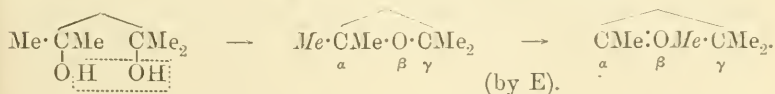


The changes observed in the formation of pinacolins from pinacones, of benzoic acid from benzil, &c., are readily explained on assumptions which the author has not been the first to make, and are doubtless closely related to those exhibited by orthodiketohexamethylene compounds (Zincke, *Ber.*, 1888, 21, 2381, &c.) and by carbohydrates in presence of alkali (Lobry de Bruyn, *Rec. Trav. Chem.*, 1893, 14, 203—216, &c.). In all these cases, it will be noticed that the change occurs at a point where it is possible that a ring compound of the

type  $-\text{R}_\alpha \triangle \text{O} \text{R}_\beta$  may be produced.

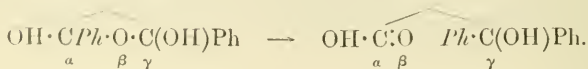
The simple change of  $\alpha$ -glycols may be taken first. It is well known that, under conditions which cause the production of oxides from  $\gamma$ - and  $\delta$ -glycols, the  $\alpha$ -glycols yield either unsaturated alcohols (in the normal manner), aldehydes, or pinacolins, according to their constitution. Hence the production of aldehydes or pinacolins from  $\alpha$ -glycols may be preceded by the formation of the corresponding unstable "ethylene oxides," when the course of change becomes abundantly clear.

With this assumption, the change of pinacones into pinacolins is seen to be in complete accordance with the author's views. Thus



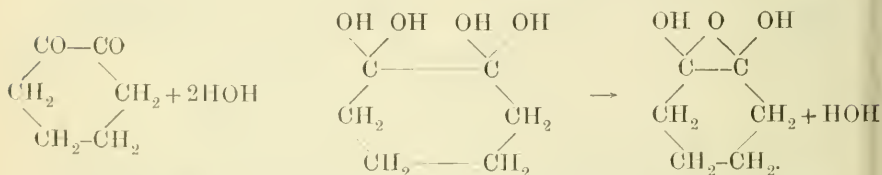
In like manner, as has been pointed out apparently for the first time by Armstrong and Groves (Miller's *Elements of Chemistry*, iii, 787), the production of benzoic acid from benzil is possibly preceded

by that of an oxide of the formula  $\begin{array}{c} \text{OH} \\ \diagup \\ \text{Ph} \cdot \text{C} \cdot \text{O} \\ \diagdown \\ \text{Ph} \cdot \text{C} \cdot \text{OH} \end{array}$ . The subsequent change may, for clearness' sake, be written as follows.

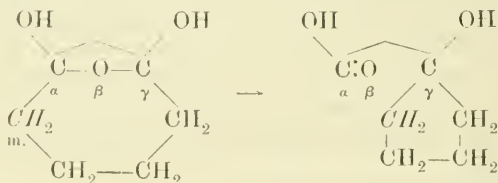


that is, affording benzoic acid,  $\text{Ph}_2\text{C}(\text{OH}) \cdot \text{COOH}$ .

A similar change in an orthodiketohexamethylene derivative [would afford an  $\alpha$ -hydroxypentamethylenecarboxylic acid, one portion of the chain functioning as M in form E. The simplest possible case of this change may be here shown.



Then, as above, for clearness, the final change may be represented as follows.



#### *Substitution in Benzenoid Compounds. The Meta Law.*

Perhaps the only attempt made to discuss the question of substitution in benzenoid derivatives from a broad standpoint was that of Armstrong's in the paper already referred to at the commencement of the present contribution (Trans., *loc. cit.*). In order to account for the fact that, whereas ortho- and para-derivatives are almost the only products when certain mono-derivatives of benzene are acted on by substituting agents, and that mono-derivatives, notably those containing acid radicles, yield chiefly meta-derivatives, the following suggestion was made. Armstrong supposed that the difference in behaviour between the two classes of mono-derivatives is attributable to the different manner in which they form additive compounds, and that where meta-derivatives are produced, initial combination of the side group with the reacting agent took place and was followed by an isomeric change resulting in substitution in the meta-position with

regard to the first group. The view was also advanced that para-derivatives were for the most part attributable to isomeric change.

Armstrong's explanation of the production of meta-derivatives has recently been revived by Collie (*Trans.*, 1897, 71, 1018); but Collie's explanation of this point fails, in the author's opinion, to account for the fact that many benzene derivatives substituted in the side group, such as phenylsulphamic acid, phenylnitramine, &c., yield, not meta-derivatives by isomeric change, but only ortho- and para-derivatives. Some explanation, therefore, other than Collie's in its original form, must be introduced in order to make the whole consistent.

The following view, a modification of Armstrong's, appears to put the matter in a perfectly consistent manner. The difference in behaviour between the two classes of benzenoid mono-substitution derivatives may, in part, be explained on Armstrong's hypothesis with the help of the principles advanced in the present paper.

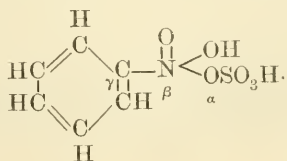
Armstrong's view as regards the production of ortho- and para-derivatives is in complete accordance with these principles. It is, in fact, only the formation of large quantities of meta-compounds which at present requires further discussion, and isomeric changes, such as that of phenylsulphamic acid into anilineorthosulphonic acid and parasulphonic acid successively, have already been brought into line with other isomeric changes.

The rule of Crum Brown and Gibson (*Trans.*, 1892, 61, 367) is an empirical one and does not attempt to offer any explanation; hence it is unnecessary to discuss this particular point fully. It may be said, however, that the rule does not apply to all cases, and where it does apply, it can be demonstrated that the constitution of the mono-derivative may be expressed by the formula  $\text{Ph} \cdot \text{R}_1 : \text{R}_2$ , so that it is in a sense unsaturated in the side group (compare Collie, *loc. cit.*).

It will be most convenient to discuss this question with reference to a special case, and the sulphonation of nitrobenzene will therefore be chosen as a fairly suitable one.

There can be little doubt that, in nitrobenzene, the nitrogen is pentad, and the only likely form in which the nitro-group can be written is  $-\text{N} \begin{smallmatrix} \text{O} \\ \text{O} \end{smallmatrix}$ .

The group is therefore of an unsaturated type, and nitrobenzene might therefore be expected to form an additive compound with sulphuric acid, and which would have the constitution

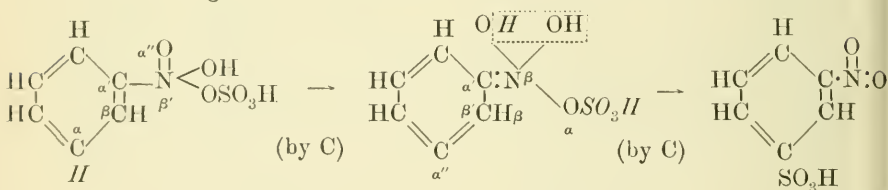


In this additive product some initial alteration of structure must occur before the sulphonic group can become attached to any carbon atom of the benzene nucleus without causing simultaneous separation of the nitro-group, and, although the change may, in accordance with the foregoing principles, be supposed to occur in at least three different ways, any simple change, not involving the production of new ring compounds, or the occurrence of polymerisation must result in the production of a metanitrobenzenesulphonic acid.

Thus, one of the following initial changes may occur.

- (1) Migration of the OH group.
- (2) „ of the O·SO<sub>3</sub>H group as a whole.
- (3) „ of a hydrogen atom of the ring, in the meta-\*position with regard to the side group.

Of these, (3) is the most simple to represent, and as it is probably the correct one, it will therefore be chosen to explain the possible series of change.



It is possible that, simultaneously with the formation of products of addition to the side group, addition to the benzene nucleus occurs, when, as usual, ortho- and para-derivatives will, for the most part, be produced. Further, it is probable that every possible additive compound is formed in slight amount, and, as in all such cases, it is only the great preponderance of one or two substitution derivatives which requires explanation.

The result of the immediately preceding discussion may be formulated as follows. Where a substitution product is formed by isomeric change of a product of addition or substitution on the side chain, in which the substituting radicle is separated from the benzenoid nucleus by two intermediate atoms, a meta-substitution derivative must be produced, or replacement of the side group by the new substituting radicle will occur (that is, with the reservations already alluded to).

The production from aniline derivatives, under some conditions, of ortho- and para-sulphonic acids only, and, under others, of meta-acids only, is doubtless accounted for by the fact that it is possible to form,

\* Migration of any other H atom into the side group is manifestly impossible, unless scission occurs. Moreover, it seems probable that, in many cases, migration of the meta-H-atom into the side group takes place as the initial step. Just as, for example, it is probable that migration of a hydrogen atom into the nitro-group of nitromethane occurs before the latter is brominated, that is, the substance reacts in its tautomeric form.

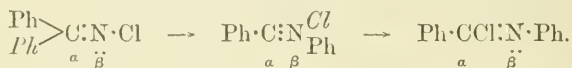




substances which undergo the above transformation exhibit a great tendency to polymerise or form double molecules, as, for instance, hydrogen cyanide, sulphites, and oximes.

A detailed series of examples of changes dependent on type X seems unnecessary, as its mode of application would be exactly similar to those employed in the more general  $\alpha\gamma$ -change. It may be of interest, however, to note that changes such as that of benzophenone-oxime into benzanilide and of amides into amines (Hofmann's reaction) are probably of this kind, although some of them may be represented by means of type E without difficulty.

Thus the change of benzophenone-oxime chloride may be written



### Conclusion.

The author has chosen, as far as possible, examples of isomeric change in which it is not sufficient to assume successive addition and subtraction of the element of the solvent or other substance within the sphere of action. The employment of such an assumption would, of course, be of great value in many cases, and possibly this process is a partial factor in some of the examples which have been given in this paper.

The question of the "residual affinity," exerted by many elements, has been but briefly touched on, and, no doubt, in extending the principles which the author is here endeavouring to introduce, this point must receive far more attention than has been devoted to it in the present paper.

It would, perhaps, be not unwise to draw attention to a factor of some importance with regard to the isomeric changes represented by the most general type A. It has already been assumed that a species of dissociation is accountable for the change which occurs, and a glance at Figs. 1 and 2 will make it clear that it is only necessary to imagine dissociation between the labile group and the atom to which it is attached, at the instant when the change actually takes place in the molecule, and it is possibly due to the attractive influence of the  $\gamma$ -atom at the period of the disturbance, where the labile group is brought under its direct influence. Thus the dissociation between Ra and M is probably only a temporary one, and it is not necessary to assume that any extensive dissociation exists, except at the instant of change. Further, a consideration of the diagrams, and the methods by which the types dependent on A<sub>1</sub> were derived from the latter, makes it clear that only one change at a time must be supposed to occur. Were the dissociation extensive and permanent,

two changes might go on simultaneously and the generalisation would be inapplicable; hence changes in electrolytically dissociated substances, or where violent action and extensive charring occurs (involving, say, complete dissociation of two or more portions of a molecule simultaneously), may result in interchange of groups not in  $\gamma$ -positions, as in B. Such changes, therefore, should be as far as possible excluded in the consideration of the applicability of the foregoing generalisation.

It appears likely that the use of the generalisation here advanced will be of value in connecting a large number of apparently independent types of change, and that its employment may serve as a means of elucidating the course of many changes hitherto regarded as extraordinary or obscure. Further, it may appropriately be pointed out that some supposed instances of isomeric change, incompatible with this generalisation, have recently been disproved by Victor Meyer and his collaborateurs.

In conclusion, I beg to thank Dr. Collie and Dr. Kipping for much kindly criticism and advice during the elaboration of this paper.

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### XLVIII.—*The Carbohydrates of Barley Straw.*

By C. F. CROSS, E. J. BEVAN, and CLAUDE SMITH.

IN the summer season of 1897, we have carried out the investigations suggested by the results of our previous work, namely, a comparison of the stem-tissues of the plant grown (1) under normal conditions, with that grown (2) under the abnormal condition induced by removing the ears when in full flower. The plants were cut at the usual harvest period, the ripe ears were removed from the former, and the stem-tissues of both were investigated by the methods previously described. It is hardly necessary to premise that the experimental plots were selected so that all other conditions of growth may be considered as having been equal, and therefore that the only variant is the suppression, in the case of (2), of the seed-bearing organs. The result of this variation, in regard to the most important of the factors under investigation, was mainly negative; the proportion of carbohydrates yielding furfuraldehyde ('furfuroids') to total carbohydrates was not affected, neither was the relative resistance of the two main groups of carbohydrates to hydrolysis with alkalis.

\* For these investigations, we were again able to avail ourselves of the experimental barley plots of the Crawley Mill Farm of the Royal Agricultural Society.

On the other hand, the plant, with its energies relieved of the work of producing seed, made but little advance towards maturation; the 'cellulose' and 'permanent tissue' constants, remained very much as at the flowering period, and correlatively the stem-tissues contained a larger proportion of carbohydrates capable of yielding to hydrolysis with acid and alkali.

In reference to the comparative external features of the growth of the plant in the experimental plots, the following are the notes supplied to us by Mr. J. J. Forrester, the manager of the Royal Agricultural Society's farm, who kindly undertook the control of the cultivation experiments. "The general tendency on the plots when the ears were clipped was to throw up fresh shoots at the bottom. . . . All the plants from which the ears had been removed developed a striking rigidity in the stem, and gradually assumed a somewhat withered appearance. . . . These did not ripen so fast as those growing under normal conditions, and at the time of cutting were distinctly greener than the others."

The following are the results of the laboratory investigation of the stem-tissues, harvested as described.

	Plants grown normally.	Plants grown with ears removed.
Total dry matter .....	86.0	83.0
,, nitrogen .....	0.6	0.9
,, mineral matter (ash) .....	8.7	6.0
,, furfuraldehyde.....	13.9	13.2
,, "permanent tissue" .....	61.6	53.5
Furfuraldehyde from "permanent tissue"	16.0	15.0
Residue from alkali hydrolysis .....	50.9	42.6
Cellulose .....	43.3	33.0
Residue from acid hydrolysis .....	54.1	48.9
Furfuraldehyde from above residue ...	5.7	5.9

The products of hydrolysis by acid were subjected to fermentation with yeast in neutralised solution; the cupric reduction and furfural constants were determined before and after fermentation, the numbers being calculated to the original 'organic' solids of the solutions. The following results were obtained.

*Acid Extract from Plants of Normal Growth.*

Alcohol produced, 11.1 per cent.

	Before.	After fermentation.
Cupric reduction (dextrose = 100)	86.8	49.6
Furfuraldehyde .....	24.7 per cent.	16.9 per cent.

*Acid Extract from Plants of Abnormal Growth.*

Alcohol produced, 18.9 per cent.

	Before.	After fermentation.
Cupric reduction (dextrose = 100)	83.3	45.0
Furfuraldehyde .....	22.4 per cent.	17.0 per cent.

The only point of difference to be noted is the increased production of alcohol in the second case.

In all those constants which define the relationship of the furfuroids to the hexose-carbohydrates of the plant, no differences of any moment are observable.

In those constants which define to a certain extent the secondary changes summed up as 'maturation,' which consist, in large measure, of condensation changes with production of the more resistant forms of tissue-carbohydrates, the laboratory investigation confirms the observations of the agriculturist in regard to the history of the growth of the plants; the 'ripening' of the stem-tissue was largely arrested by the suppression of the seminal function, and the chemical results of this are that the carbohydrates remain in a more digestible condition, that is, a larger proportion are in the condition to yield to hydrolytic action; we may also note that the non-depletion of the stem as regards nitrogenous constituents is shown in the higher proportion (50 per cent.) of total nitrogen.

It will be remembered that the original purpose of these investigations was to obtain evidence as to the conditions of formation of furfuroids in the plant. We have already studied the plant under the widest range of variations of conditions of growth as regards soil, nutrition, and climate, and now we have added the effect of varying an essential physiological factor. In no case have we found any differentiation of the furfuroids from the hexose carbohydrates, such as to warrant the conclusion that they are formed from the latter by external chemical change (oxidation); or, to express the conclusion in positive terms, we find that the furfuroids rank with the hexose carbohydrates as primary products of assimilation. We are here confronted with a critical difficulty. The furfuroids of the cereal straws in their mature condition are undoubtedly (condensed) aldoses, and either pentoses or pentose derivatives. But an accumulation of physiological evidence has established that the pentoses do not rank with the hexoses in relation to assimilation, or to the constructional metabolism of the plant. The pentoses, unlike the hexoses, do not occur as such in the plant; the current theories as to the mechanism of the formation of carbohydrates in the growing cell also exclude any products intermediate



between those of the dimensions  $C_3$  and  $C_6$ . In our researches, we have given weight to this apparent conflict of evidence, and have searched for such evidence (1) as would differentiate the furfuroids of the cereal straws from the pentoses proper (or pentosans), (2) as would indicate a transition from the hexose to the pentose series. In both directions, we have arrived at results, but as these have been fully stated in our previous communications, it is needless to reproduce the evidence in detail here, especially as much fuller investigation is needed before the matter can be considered as finally settled.

On one point, however, we have some fresh evidence confirmatory of that recorded in our previous communication (Trans., 1896, 69, 1604). Whereas, under all conditions of hydrolysis by alkali, the two groups of carbohydrates are equally attacked, the same proportion between them being maintained in the residue of severe alkali treatment (cellulose), as in the intermediate stages, the attack by acids is more selective. This will be apparent at once from the results obtained with barley of 1897, taken (*a*) in the flowering stage and (*b*) after harvesting.

The conditions of acid treatment were as follows. Two hours boiling with dilute sulphuric acid (1.0 per cent.  $H_2SO_4$ ) under ordinary atmospheric pressure. The furfuraldehyde in the dissolved products was estimated and calculated to the 'total organic matter' in solution. Whereas in (*a*) the proportion was 12.3 per cent., in (*b*) it amounted to 33 per cent. (average number for the two crops). Now the number for (*a*) differs but little from that of the entire plant substance (10 per cent.); in other words, in the earlier stages of growth, the two groups of carbohydrates are equally attacked by acids. In (*b*), on the other hand, the furfuroids are attacked by preference; and in our previous papers we have dealt with a number of cases, where, with furfural numbers at 40—50 per cent. of the dissolved solids, the attack by acid hydrolysis is more exclusively confined to the furfuroids. These results indicate that the furfuroids undergo some constitutional change with age by which they are differentiated from the hexose groups with which they are associated in intimate union. This fact is emphasised by the results of alcoholic fermentation. It is now well established that the pentoses are not fermented by yeast. In our last paper, we dealt with the causes of a disappearance of pentoses in the fermentation of mixtures of pentoses and hexoses, under certain conditions of the action of the yeast cell; we found that this occurred when there was a relative starvation of the latter, but *not* when the fermentation was vigorous and rapid.

The results given below of the fermentation of the acid extract (after neutralisation) of the immature plant (*a*), must be

compared with those previously recorded (see above) for the matured plants.

Alcohol produced, 19·4 per cent.

	Before.	After fermentation.
Cupric reduction (dextrose = 100)	49·6	0·00
Furfuraldehyde ... ..	12·3 per cent.	2·9 per cent.

The fermentation in this case was complete so far as regards the fully hydrolysed molecules; and the small proportion of residual furfuroids which are present in the still condensed form cannot be set down to resistance to the attack of the organism. Moreover, as the proportion of furfuroids to total carbohydrates was relatively low, the disappearance of 77 per cent. during fermentation is the more noteworthy.

These results add further confirmation to the conclusion that a constitutional change of the furfuroids accompanies maturation; a change from that of a furfural-yielding carbohydrate susceptible of fermentation by yeast to that of a pentose or pentosan. We have no evidence that this change is influenced by external conditions of growth, and there is nothing to show that the change is one of oxidation from without.

The only hypothesis we have so far found to be consistent with all the evidence is that of an internal constitutional change, the terminal  $\begin{smallmatrix} \text{CH}_2\cdot\text{OH} \\ | \\ \text{CH}\cdot\text{OH} \end{smallmatrix}$  groups of a hexose being rearranged with formation of a carbonyl group, that is, a process of internal oxidation. We have not yet sufficient positive evidence to take this suggested explanation out of the region of hypothesis; but our investigations in this direction are being continued, and we hope in a short time to communicate the results of a comprehensive study of the interaction of the hexoses with hydrogen peroxide, bearing directly on the questions herein discussed.

We wish to again express our obligations to Messrs. A. and E. Voelcker, whose laboratory has been at our disposal for the conduct of the chemical work; and to Mr. Forrester for his kind co-operation in the cultivation experiments.

## XLIX.—*Reactions of the Carbohydrates with Hydrogen Peroxide.*

By C. F. CROSS, E. J. BEVAN, and CLAUDE SMITH.

HOWEVER obvious it may appear that the simpler carbohydrates would react with hydrogen peroxide under certain conditions, the matter has

been but little investigated. The only reference we can find dealing specifically with the subject is contained in a paper by C. Wurster (*Ber.*, 1887, 20, 2631), where the question of reaction is dismissed with the negative remark that glucose and cane-sugar are comparatively resistant to the action of the peroxide.

The recent series of researches of H. J. H. Fenton on the oxidation of tartaric acid by hydrogen peroxide has disclosed several points of especial interest in regard to the mode of action of the latter, more particularly the oxidation of the residue  $-\text{CH}(\text{OH})\cdot\text{CH}(\text{OH})-$  to  $-\text{C}(\text{OH})\text{:C}(\text{OH})-$ , and the dependence of this oxidation on the presence of soluble iron compounds (*Trans.*, 1894, 65, 899; 1895, 67, 48; 1896, 69, 546), and the results certainly suggest fruitful extension of the method to other hydroxy-compounds. In correspondence with Mr. Fenton, we undertook the preliminary investigation of the behaviour of typical carbohydrates with the peroxide under similar conditions of treatment, and the results of our observations are here briefly recorded.

It is recognised by chemists on general grounds, as it is more positively held by physiologists, that the carbohydrates are oxidised in the living cell by processes of varying intensity; but it must be admitted that very little direct light has yet been thrown on the actual mechanism of such processes. Our laboratory processes of oxidation are of two kinds, namely, 'constructive' oxidations of the hexoses to monocarboxylic acids (by bromine) and dicarboxylic acids (by nitric acid), and destructive oxidations to products of lower molecular weight, for instance, by alkaline cupric oxide, permanganates, and hypochlorites. The latter are so complex in character that they at present occupy only a subordinate place in the systematic investigation of constitutional problems, neither are such methods calculated to directly elucidate physiological problems.

Oxidations of the hexoses by hydrogen peroxide, on the other hand, such as we are about to describe, are of the kind which may be fairly presumed to take place in the plant; for although the existence of this particular 'kathoxide' in the plant cell may be difficult of proof by application of the ordinary reagents, it is generally admitted that the 'active oxygen' of the cell must in part at least take this form (A. Bach, *Compt. rend.*, 1894, 119, 286).

The dependence of such oxidations on a particular third substance, acting simultaneously, has not been assumed, nor, so far as we know, surmised by physiologists. As we are now able to show that iron salts have a specific influence in exciting or determining these oxidations, these investigations involve direct inquiry into the functions of the inorganic or ash constituents of plants. It must be admitted that the enormous accumulation of facts in this province, in the form

of analytical results, has as yet but little other than a general significance to the physiologist. It would appear that the inorganic salts must directly affect the many processes of hydrolysis and condensation going on in the plant; but their influence as determining or modifying oxidising actions, in which from their nature they can only play the subordinate part of "catalysts," is hardly to be predicted on such definite grounds as "the nature of things." There may, perhaps, be some suggestions, in the nature of the iron salts, of the mechanism of their action as the *tertium quid* in effects of oxidation; and this matter is dealt with by Mr. Fenton in a note communicated simultaneously with this paper. But similar reasons could not obtain for a compound such, for example, as phosphoric acid. And yet it has been already observed, as an "extraordinary circumstance," that in the oxidation of acetone by hydrogen peroxide (to the 'cycloacetone peroxide'), a small quantity of phosphoric acid determines the reaction, which does not take place with the pure reagents (Wolffenstein, *Ber.*, 1895, 28, 2267). A reaction of this kind had no obvious bearing on physiological problems; but in connection with the subject of this paper, it is a significant extension of the probabilities under discussion.

One other consideration we have to note by way of prelude to a brief account of the experimental results which we have obtained. These investigations arise out of our continuous search for a solution of the problems of the origin in the plant of (1) the lignocelluloses, and (2) the carbohydrates yielding furfuraldehyde. As a working hypothesis, it has been assumed that both groups of tissue constituents are formed from the normal carbohydrates. This hypothesis, taken together with the assumption that "the plant can do everything," has been, and is, a very unsatisfying resting place. It must be admitted that the systematic study of the carbohydrates, notwithstanding its rapid advance, has not afforded any suggestion as to the actual mechanism of such transformations. Fenton's researches coming at a time when we had exhausted the more obvious directions of indirect inquiry, imported entirely new suggestions; the first of which is that, as in the dicarboxylic hydroxy-acids, so in the carbohydrates, there is a direct passage to unsaturated compounds by way of oxidising processes. To prove this suggestion, and to open out these physiological problems from the more positive chemical standpoint, has been our first and main purpose.

This being merely a preliminary communication, we shall limit it to a brief explanation of the purpose and aims of the investigation, and an equally brief account of the experimental results so far obtained.

In some respects, the most striking result is the verification of Wurster's statement as to the comparative resistance of the hexoses (and cane-sugar) to the action of hydrogen peroxide, with the exten-



sion of Fenton's observation that the equilibrium is upset by the addition of ferrous salts in such small proportion as 1/10000 ( $\text{Fe}''$ ) of the weight of the solution. This has been repeatedly verified. The obvious methods of noting equilibrium under the former condition are (1) absence of any change of temperature; (2) no change of rotation; (3) survival of the peroxide after prolonged contact. The addition of a ferrous salt—we have usually employed the sulphate—is followed by changes in all three directions. Unfortunately, owing to the turbidity occasioned by the addition of the iron salt, the intermediate stages of the reaction cannot be followed by polarimetric observation. The rise of temperature and disappearance of the peroxide are proportional in rate and degree to the concentration of the solutions.

With 4 per cent. solutions of the carbohydrates, and the peroxide sufficient to supply 1 atom of oxidising O per molecule ( $\text{C}_6\text{H}_{12}\text{O}_6$ ), a rise of temperature from  $15^\circ$  to  $30^\circ$  takes place in a period of 1—2 hours; with 10 per cent. solutions, on the other hand, the proportions of the reagents otherwise remaining the same, the temperature will rise to  $50$ — $60^\circ$ ; in the latter case, there is considerable evolution of gas. By comparing these effects with those obtained with the peroxide and iron salt alone, that is, in absence of the carbohydrate, allowance can be made for the relatively small evolution of heat due to the exothermic resolution of the peroxide itself; moreover, the latter is rapidly completed, and is accompanied by evolution of oxygen, whereas in presence of the carbohydrate, some considerable time always elapses before exothermic reaction sets in.

These effects were indirectly verified by taking advantage of the observation that by using only fractional proportions of the peroxide, products were formed which, whilst they have most of the properties of the glucoses (see below) resisted fermentation.

In the subjoined series of experiments, this residue was determined in terms of cupric-reducing power, and calculated to the original carbohydrate (dextrose).

To 25 c.c. of a 5 per cent. solution of dextrose was added in each case 20 milligrams of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ . To each of three such quantities, hydrogen peroxide was added representing 1/40 to 1/10 atom of oxygen per mol. of  $\text{C}_6\text{H}_{12}\text{O}_6$ ; a fourth (blank) received none. After reaction, they were fermented by yeast, and the residual 'sugar' determined as indicated.

	Proportion of peroxide $\text{O} : \text{C}_6\text{H}_{12}\text{O}_6$ .	Residual sugar (Calc. from CuO reduction).
1.	None	None
2.	1/40	9.2 per cent.
3.	3/40	14.0   ,,
4.	4/40	20.0   ,,



These results will be referred to subsequently, as they have a bearing on the theoretical aspect of the reactions.

We shall not further discuss this side of the reaction. It is sufficiently proved that some third substance is necessary to determine reaction, and that iron salts have this function is a point which may be emphasised from its obvious physiological significance. Other compounds will no doubt be found which exert a similar influence, and it is quite probable that, corresponding with differences in chemical function, we may be able to establish specific differences in regard to the products formed in the reactions; this will be more clearly seen when the nature of the products and of the reaction has been more closely described. Operating in dilute solutions (4 per cent. of the hexoses), we may premise that there is very little effervescence or other indication of destructive oxidation, and after making comparative experiments at 0—4°, we find the ordinary atmospheric temperature to be the most favourable for the purpose. The proportion of iron (Fe) taken is usually 1/10000 the weight of the solution and in the form of ferrous sulphate. The peroxide is added gradually, and in proportion calculated to, say, 1 atom of 'oxidising oxygen' to each mol. of  $C_6H_{12}O_6$ , that is, about 9 per cent. by weight.

After the reaction is complete and the peroxide has entirely disappeared, the yellowish-brown solution is acid to the taste. The following numerical results obtained with a dextrose solution (4 per cent.), treated under the conditions above specified, will give a general idea of the products of the reaction.

Total 'organic' solids (dried at 105°), 87.7 per cent. of original.

Acidity, equal to 1/5 normal acid.

CuO reduction (calc. to organic solids), 96.5 (dextrose = 100).

Sp. rotation,  $[\alpha]_D = 33.8^\circ$ .

Furfuraldehyde, 3.75 per cent.

*Reaction with phenylhydrazine acetate* takes place in the cold, the products having all the characteristics of the osazones. The yield of insoluble osazone in this case was 14 per cent. of the weight of the original dextrose. After recrystallisation from dilute alcohol, it melted at 194°, and on combustion yielded N = 19.8 per cent. The filtrate from the osazone thus formed in the cold, and containing a calculated excess of phenylhydrazine, gave only a slight further precipitate on heating at 100°.

It would appear, therefore, that the original solution contained but little residual dextrose. After boiling with hydrochloric acid (added to the proportion of 15 per cent. HCl), the cupric reduction was in effect lowered from 96 to 5.7 (dextrose = 100). We will deal at once with a suggestion which obviously arises from these numbers, namely, that

the characteristic products which react with the phenylhydrazine in the cold are of the type of glucosone (or oxyglucose).

The solution was treated with zinc and acetic acid, and the reducing action allowed to continue some hours; the cupric reduction was thereby but little affected, falling from 96.5 to 95.4. The solution still gave the osazone in the cold, but the yield was reduced from 14 to 6.4. After hydrolysing, however, by boiling with sulphuric acid (2 per cent.,  $\text{H}_2\text{SO}_4$ ), the original yield of 14 per cent. was obtained, and the compound formed had the same properties. The products are by these properties differentiated from the 'osones.'

The above constants are sufficiently definite as a basis for a preliminary investigation of the nature of the reactions. Thus it might be presumed that, in the event of oxidation occurring in the case of an aldose, the first point to be attacked would be the terminal aldehydic group. The numbers above cited are sufficient to show that, although profound changes have been determined, they are not at all of the order of such simple oxidation. These numbers, representing the effects due to 1 atom of oxygen, serving as a basis of comparison, experiments were made with 2, 3, and 4 atoms of oxygen, and on comparing the constants it was found that the effects produced were by no means proportional to the amount of oxygen. Thus the following constants were determined in the solution obtained by treating the aldose with 2 atoms O (as  $\text{H}_2\text{O}_2$ ), all other conditions remaining the same.

Total organic solids, 85.5 of original.

Acidity equal to 1/5 normal acid.

CuO reduction (calc. to organic solids), 86.5 (dextrose = 100).

Sp. rotation,  $[\alpha]_D = 16.5^\circ$ .

Furfuraldehyde, 3.75 per cent.

Osazone (in the cold), yield 22.6 per cent.

The additional quantities of oxygen failing to produce proportional effects, it was concluded that the characteristic products which react with phenylhydrazine in the cold, and also reduce Fehling's solution powerfully in the cold, although highly reactive substances, will resist the action of certain oxidising agents. We found, in fact, that they were not oxidised even by prolonged treatment with bromine, although some bromine is taken up and hydrogen bromide produced; calculating this to oxygen, it amounts on the average to 5—7 per cent. of the weight of the original carbohydrate, that is, about  $\frac{1}{2}$  an atom of oxygen, but the cupric reduction is lowered not more than 20—25 per cent. and the solutions still give the characteristic reactions with phenylhydrazine. Even on warming with bromine, the oxidation is not carried much farther.

As regards the most characteristic of the products, therefore, the results bear no direct proportion to the amount of the oxidising agent employed, and that is, to a certain extent, explained by the points of divergence in properties between these products and the normal carbohydrates.

When proportions less than the 1 atom of oxygen were used, the results still failed to show any quantitative sequence downwards.

Our friend, Dr. R. S. Morrell, was kind enough to carry out an experiment for us in which 40 grams of dextrose were treated with the peroxide in the proportion of 1/10 atom of 'oxidising oxygen' per mol. of  $C_6H_{12}O_6$ . We were anxious to have our results confirmed by an independent observer, and Dr. Morrell's experience in Professor Fischer's laboratory adds value to the confirmation. He obtained from the products of the reaction 8 grams of the osazone formed in the cold, that is, a yield similar to that which we obtained when using twenty times this proportion of oxidising oxygen. In fractionating the osazone, he also confirmed our results in regard to its being a mixture of two compounds or groups of compounds.

(a) Soluble in hot water, m. p.  $130^\circ$ .

(b) Relatively insoluble, m. p.  $185^\circ$ .

If, in place of regarding these effects as an oxidation of 40 grams of the hexose by the peroxide in the proportion of 1/10 atom of oxygen, we interpret it as resulting from the attack of 4 grams by 1 atom of oxygen per 1 mol. of  $C_6H_{12}O_6$ , the effects are not accounted for; but such an interpretation is excluded by an examination of the whole series of results.

We have now to show how far the reaction is elucidated by the other products, which have, so far, only appeared in statistical results.

#### *The Furfural-yielding Compounds*

have not been isolated. It is probable that the furfuraldehyde obtained on boiling with hydrochloric acid results from a complex decomposition of the characteristic ketonic products, for, like these, the parent 'furfuroid,' is not oxidised by bromine, neither is it separated amongst the acid products about to be described. We have, therefore, nothing to identify it with the better known furfuroids, that is, with the pentoses, on the one hand, and glycuronic acid on the other. The formation of a furfural-yielding group is of some physiological significance, for the reasons given in the earlier part of this paper.

#### *Acid Products.*

The most characteristic of these is a substance which is precipitated as a lead salt in presence of acetic acid. The salt thus obtained has

been analysed several times after recrystallisation from highly dilute nitric acid, and the numbers obtained correspond with those for the lead salt of tartronic acid. The yield has also been several times estimated, the numbers indicating from 7 to 10 per cent. of the acid calculated to the original carbohydrate.

In addition to this dicarboxylic acid, monobasic acids are separated in some quantity on distilling the solutions. Estimated in terms of normal alkali by comparison with the acidity of the original solutions, the volatile acids amount to about one-half.

By redistillation after oxidation with neutral permanganate, these were resolved into acetic acid, resisting the oxidation, and formic acid oxidised. The quantities calculated to the original carbohydrates vary from 3—7 per cent. of acetic and 13—18 per cent. of formic acid.

The loss of volatile acids on evaporating the solution appears to correspond with the deficiency in the 'total solids' after reaction; but this point need not be pressed too closely, as it has not been ascertained what dehydration the ketonic products undergo by 'drying' at 105°. These statistical numbers, however, generally confirm the observation that the reactions, under the usual conditions, are not marked by destructive oxidation (to  $\text{CO}_2$ ).

It is, of course, to the acid products that we first look in summing up the results to a quantitative account of the reactions. The acidity of the oxidised solutions, as originally obtained and determined by direct titration, is approximately accounted for in terms of the two groups of acids estimated as stated; there appears to be no subsequent production of volatile acids by changes in the products during the distillation. On the first obvious assumption that the  $\text{COOH}$ -groups are produced from the  $\text{COH}$ -groups of the aldose, we find in many cases that, although this accounts for all the oxygen added as  $\text{H}_2\text{O}_2$ , it leaves us with 60—70 per cent. of the carbonyl oxygen of the original hexose, measured in terms of cupric reduction, and confirmed by the reactions with phenylhydrazine.

It appears, therefore, from this preliminary survey of the products that the reactions are not of such 'obvious' simplicity, but are complicated by internal rearrangement of the hexose molecule; a conclusion which appears necessary to explain the results of the fermentation experiments described in the earlier part of this paper. This conclusion is confirmed by the observation that the solutions give a pronounced iodoform reaction, as do also the acid distillates. We have not as yet further identified the methylated derivatives thus shown to be formed; their production is a sufficient index of the factor of rearrangement which has to be taken into account.

Before dealing finally with the issues raised by the empirical study



of the 'constants' of the reactions, we have to contrast with the above *the results obtained with levulose and cane-sugar*.

The solutions obtained from the ketose have generally the same characteristics as those from the aldose, but with the following specific and noteworthy difference: *furfuroids are not formed*, the solutions giving traces only of furfuraldehyde, the *total acidity* of the solutions is less, and the dicarboxylic acid is proportionally small in amount and appears to be an acid of higher molecular weight. On the other hand, the cupric reduction is relatively high, and the yield of osazone in the cold is also high, exceeding, in many cases, 50 per cent. of the weight of the solids in solution.

The following observations on the osazone obtained from the hexose, treated with 1 atom of oxygen, as  $H_2O_2$ , are of interest. As obtained from the original solution, the osazone melted at  $195^\circ$ . After prolonged digestion with excess of bromine and removal of the bromine, the solution gave the same osazone in the cold. On combustion, it gave  $N = 16.5$  per cent.

Treatment of the original solution with zinc and acetic acid (examination for 'osones') affected the cupric reduction somewhat (10 per cent.), and lowered the yield of the characteristic osazone from 30 per cent. to 10 per cent.; but after hydrolysing by boiling with sulphuric acid (2 per cent.  $H_2SO_4$ ), the yield of the osazone was doubled. These numbers indicate, again, that the reactions are complicated by tendencies to condensation.

In general terms, the results with the ketose sufficiently resemble those with the aldose to lead to the conclusion that the position of the typical CO-group does not exert an influence such as it does in ordinary processes of oxidation; and this confirms the previous conclusion that the reactions of hydrogen peroxide are far removed from those of simple oxidation.

*Cane-sugar* gives us a third variation in regard to the typical CO-groups of the original carbohydrate, and as the results obtained with the peroxide under similar conditions of treatment are in all respects closely similar to those with the constituent hexoses, we may conclude that hydrolysis is rapidly determined. As regards the products of the reaction, the results may be taken as intermediate between those for the constituent hexoses in those directions in which differences have been established.

As this is only a preliminary communication, we limit ourselves to the statement of typical quantitative results and general indications of the scope of the investigation. It will be seen that the main interest of the inquiry centres in the identification of the characteristic ketonic products of the reaction. Were these products of a simple nature, we should have made more progress in this direction; so far,



we have been unable to crystallise them ; we have also been unable to obtain crystalline acetates or benzoates. On the other hand, we have noted the evidence of the tendency of the products to condensation, which, so far, accounts for the difficulty of obtaining them in their simplest form.

If we are dealing with groups of the form  $-C(OH):C(OH)-$ , the anticipation with which, on the basis of Fenton's researches, we set out, many of our results, both positive and negative, are generally explained. It is clear that in the carbohydrates such groups can be formed in two ways : either from a  $-CH(OH)\cdot CH(OH)-$  residue by oxidation, or from the  $-CO\cdot CH(OH)-$  residue by a simple transposition. We may also note that, in the condensation of the pentoses to furfuraldehyde, the formation of the aldehyde is usually formulated as prepared for by a similar grouping.

The only objection in the way of these views as a working hypothesis is that it conflicts somewhat with the present view of the osazone reaction. This objection will, of course, have weight in the further prosecution of the investigation, which will involve a critical examination of the evidence in this direction ; the more so as the "osazone" reactions which we have described are both novel and characteristic.

## I.—*Properties and Relationships of Dihydroxy-tartaric Acid. Part II. Salts of the Acid.*

By HENRY J. HORSTMAN FENTON, M.A.

### *Salts of Dihydroxytartaric Acid.*

THE only salts of this acid which appear to have been examined hitherto are the sodium salt (Grüber, Barth and Kekulé), the barium salt (?) (Barth), and the ethylic salt (Anschütz). From the experiments previously recorded (Trans., 1898, 73, p. 74) on the titration of the free acid by alkalis, it is evident that the salts are extremely unstable in the presence of water at the ordinary temperature, and this circumstance probably accounts for certain discrepancies in the statements made by different authors. Mere washing with water at the ordinary temperature, for example, would cause a certain amount of decomposition into tartronate and carbon dioxide.

The titration by permanganate affords a very convenient method for studying the composition of these salts, the substance, for this purpose, being decomposed by a large excess of dilute sulphuric acid, and titrated with potassium permanganate at the ordinary temperature (Trans., 1898, 73, 167).

*Potassium Salt.*

The formation of this salt was first observed during experiments on the volumetric estimation of sodium. High results were obtained when potassium carbonate was employed for neutralising the free dihydroxytartaric acid in concentrated solutions, and these were found to be due to the separation of a certain quantity of the potassium salt along with the sodium salt. The substance is easily prepared by adding a concentrated solution of pure potassium carbonate\* in slight excess of the calculated quantity to a concentrated solution of the free acid; both solutions must be ice cold before mixing, and the mixture is allowed to stand in melting ice. The salt, which soon separates as a white, crystalline precipitate on shaking or stirring, is collected on a filter, washed quickly with ice-cold water, well drained with aid of the pump, and pressed between changes of filter paper.

The air-dried salt loses no weight when kept for several days in a vacuum desiccator.

The following results were obtained on analysis.

I. 0.3378 gave 0.2120 $K_2SO_4$ .	III. 0.3924 gave 0.2470 $K_2SO_4$ .
II. 0.4719 „ 0.2974 $K_2SO_4$ .	IV. 0.4275 „ 0.2687 $K_2SO_4$ .

These four analyses were made with distinct specimens prepared on different occasions. III was dried in a vacuum, and the others air-dried.

V. 0.5641 gave 0.3515  $CO_2$  and 0.1096  $H_2O$ .

	Found.				
	I.	II.	III.	IV.	Calculated for $K_2C_4H_4O_6 + H_2O$ .
K	28.13,	28.25,	28.21,	28.17	28.26 per cent.
C		16.99			17.39 „
H		2.12			2.17 „

VI. When heated at about  $100^\circ$  in a water oven until the weight became constant, 0.4501 substance lost  $0.1287 = 28.59$  per cent. The residue was highly deliquescent, and gave no reaction of dihydroxytartrate with sodium chloride solution.

If the salt decomposes into potassium tartronate and carbon dioxide, according to the relation  $K_2C_4H_4O_6, H_2O = K_2C_3H_2O_5 + CO_2 + 2H_2O$ , the loss should be 28.98 per cent.

VII. Decomposed with dilute sulphuric acid, and titrated with a solution of potassium permanganate containing 6.3375  $KMnO_4$  per litre, 0.1723 gram of substance required 18.4 c.c. of permanganate. Theory (as standardised by the free acid) = 18.03 c.c.

\* A product which is apparently identical in every respect is obtained by substituting potassium acetate for potassium carbonate.

VIII. 0.4525 gram of substance took 48.3 c.c. permanganate.  
Theory = 47.35 c.c.

The permanganate values are, in fact, always somewhat higher when referred to the potassium salt than when referred to the free acid. The potassium salt crystallises extremely well, and from the very close agreement of the results obtained on analysis of various specimens, it is probable that its purity is more to be relied upon, as an agent for the standardisation of permanganate solutions, than that of the free acid. The oxygen value, moreover, approaches more nearly to the theoretical (3 atoms of oxygen per molecule of acid) when the potassium salt is employed.

For the purpose of analysing other dihydroxytartrates, fresh solutions of potassium permanganate were prepared from time to time, and standardised by means of the potassium salt.

*Solution A.* [S = strength in grams of  $(C_4H_4O_8)$  per litre.]

Potassium salt.	Permanganate.	S.
I. 0.1920 gram required	21.81 c.c.	5.7309
II. 0.3970 „ „	45.05 „	5.7474
III. 0.3654 „ „	41.60 „	5.7288
IV. 0.4792 „ „	54.25 „	5.7609

(These results were obtained with three distinct specimens.)

The mean strength of A is therefore 5.7420  $(C_4H_4O_8)$  per litre.

*Solution B.*

Potassium salt.	Permanganate.	S.
I. 0.5968 gram required	59.65 c.c.	6.525
II. 0.9332 „ „	93.70 „	6.4955

Mean strength = 6.5102  $(C_4H_4O_8)$  per litre.

Standardised by means of ammonium oxalate, this solution B gave the following result.

0.8430 gram of  $(NH_4)_2C_2O_4 \cdot II_2O$  required 55.05 c.c. of permanganate.

One molecule of the potassium salt requires, therefore, 2.98 atoms of oxygen. Previous determinations with the *free acid* gave a mean of 2.89 atoms, theory requiring 3 atoms.

#### *Sodium Salt.*

According to the analyses of Grüber, Barth, and Herzig, the composition of the sodium salt dried in a vacuum is  $Na_2C_4H_4O_8 + 2H_2O$ , whereas Kekulé's results point to the composition  $Na_2C_4H_4O_8 + 2\frac{1}{2}H_2O$ .

As the exact composition of this salt is a matter of some importance, it was now prepared for investigation with great precautions against

risk of decomposition, the details of working being the same as in the preparation of the potassium salt.

The precipitated salt, after being well pressed and air-dried for about 24 hours, gave the following numbers.

- I. 0.4766 gave 0.2430  $\text{Na}_2\text{SO}_4$ .  
 II. 0.5342 „ 0.2747  $\text{Na}_2\text{SO}_4$ .  
 III. 0.4410 gram required 49.75 c.c. of permanganate (A).

	Found.	Calculated for $\text{N}_2\text{C}_4\text{H}_4\text{O}_8 + 3\text{H}_2\text{O}$ .
Na .....	16.51, 16.65	16.42 per cent.
$\text{C}_4\text{H}_4\text{O}_8$ .....	64.77	64.28 „

This air-dried salt loses weight when kept in a vacuum desiccator, the weight becoming constant after 2 or 3 days.

III. 1.2172 lost 0.0410  $\text{H}_2\text{O}$ .  $\text{H}_2\text{O} = 3.36$ .

IV. 1.8222 „ 0.0527  $\text{H}_2\text{O}$ .  $\text{H}_2\text{O} = 2.89$ .

Theory for loss of  $\frac{1}{2}\text{H}_2\text{O} = 3.21$  per cent.

The salt dried in a vacuum was also analysed.

- I. 0.4104 gave 0.2169  $\text{Na}_2\text{SO}_4$ .  
 II. 0.2265 gram required 26.3 c.c. of permanganate (A).

	Found.	Calculated for $\text{N}_2\text{C}_4\text{H}_4\text{O}_8 + 2\frac{1}{2}\text{H}_2\text{O}$ .
Na .....	17.12	16.97 per cent.
$\text{C}_4\text{H}_4\text{O}_8$ .....	66.67	66.42 „

### *Ammonium Salt.*

This was prepared in the same manner as the potassium and sodium salts, the strength of the ammonium carbonate solution being previously ascertained by titration with normal sulphuric acid. In appearance, it much resembles the potassium salt, and is slightly more soluble; it is, however, much less stable, for on exposure to the air for a day or two it turns first yellow and finally deep orange, increasing considerably in bulk.

Analysis of a pure white specimen which, after pressing, had been air-dried for about 20 hours, gave the following results.

I. 0.5693 gram, distilled with caustic soda, gave ammonia which neutralised 8.62 c.c.  $\text{N}/2 \text{H}_2\text{SO}_4$ .

II. 0.2186 gram required 27.05 c.c. of permanganate (A).

III. 0.1935 „ „ 24.0 „ „ „

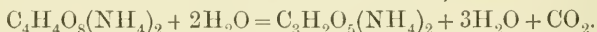
	Found.	Calculated for $(\text{NH}_4)_2\text{C}_4\text{H}_4\text{O}_8 + 2\text{H}_2\text{O}$ .
$\text{NH}_3$ .....	12.87	13.49 per cent.
$\text{C}_4\text{H}_4\text{O}_8$ .....	71.05, 71.21	71.42 „

The air-dried salt, when kept in a vacuum over sulphuric acid, loses weight very slowly and regularly, the weight not becoming constant until after about three months. The diminution in weight then amounted to about 40 per cent., corresponding approximately to a loss of  $6\text{H}_2\text{O}$ , or, if carbon dioxide is also given off, to a loss of  $\text{CO}_2 + 3\text{H}_2\text{O}$ . The residual substance was of a buff-yellow colour, and was extremely deliquescent. Heated with caustic soda solution, it evolved ammonia, but its aqueous solution gave no reaction of dihydroxy-tartaric acid either with sodium chloride or sodium carbonate.

0.2043 gram gave 31.4 c.c. nitrogen at  $17^\circ$  and 758.3 mm.  $\text{N} = 18.11$ .

A substance having the formula  $\text{C}_4\text{H}_4\text{N}_2\text{O}_4 [= \text{C}_4\text{H}_4\text{O}_8(\text{NH}_4)_2 \cdot 2\text{H}_2\text{O} - 6\text{H}_2\text{O}]$  would require 19.44 per cent., whereas ammonium tartronate,  $\text{C}_3\text{H}_2\text{O}_5(\text{NH}_4)_2$ , requires 18.18 per cent.

From this result, and from the fact that the substance gives no dihydroxytartaric acid reaction, it is probable that ammonium dihydroxytartrate decomposes when kept in a vacuum desiccator, giving carbon dioxide and ammonium tartronate,



With the object of ascertaining whether it is possible to prepare the anhydrous ammonium salt, the following experiment was made.

A solution of dihydroxytartaric acid in absolute alcohol was mixed slowly with slightly more than the calculated quantity of ammonia, also dissolved in absolute alcohol, both solutions being ice cold and the mixture kept in ice as before. The bulky, white precipitate produced was collected with the aid of a pump in an apparatus so constructed that the entering air was carefully dried, and the filtering tube kept cold; after draining as well as possible, the product was kept in a vacuum desiccator over sulphuric acid. (A portion of the freshly prepared product, dissolved in water, gave an immediate precipitate with sodium chloride solution.) The substance lost weight slowly and regularly, as in the previous case, and after 6 days it was found, on testing with sodium chloride, that it gave no reaction of dihydroxytartrate.

Another specimen was therefore prepared in exactly the same manner, washed with anhydrous ether, and examined after it had remained in the vacuum desiccator for only about 18 hours. In this case, the product gave, somewhat slowly, a slight indication of dihydroxytartrate when tested with sodium chloride, but on titration with permanganate, no definite end-point could be obtained as in the previous cases, the colour being slowly discharged for upwards of an hour. A similar behaviour is observed in other cases (for instance, with the dried barium salt; see below) where the product contains tartronate.



It appears, therefore, that precipitation of the alcoholic solution of dihydroxytartaric acid by alcoholic ammonia gives rise to the anhydrous ammonium salt, which may be  $C_2(OH)_4(COONH_4)_2$  or  $C_2O_2(COONH_4)_2$ ; but that this salt undergoes decomposition when dried in a vacuum desiccator. This fact, and that the hydrated salt,  $C_2(OH)_4(COONH_4)_2 + 2H_2O$ , can easily be isolated, and is stable, at any rate for a day or two, is of interest in comparison with the behaviour of ammonium glyoxylate, the formula of which corresponds to the dehydrated or ketonic form of the acid.

### *Lithium Salt.*

Commercially pure lithium chloride, after being further purified by treatment with a mixture of absolute alcohol and ether, was dissolved in water and mixed with a solution of potassium dihydroxytartrate in about the calculated quantity, both solutions being ice cold and the mixture kept in ice. The lithium salt, which separated almost immediately as a crystalline precipitate, was collected, washed repeatedly with ice cold water and pressed, as in the previous cases.

The salt is very sparingly soluble in water, but is more soluble than the sodium salt. When well stirred with water and filtered, the clear filtrate gives a distinct precipitate with strong solutions of sodium chloride.

The air-dried substance gave the following results on analysis.

I. 0.4896 gram required 56.5 c.c. of permanganate B.

II. 0.3019 gave 0.1407  $Li_2SO_4$ .

	Found.	Calculated for $Li_2C_4H_4O_8 + 2\frac{1}{2}H_2O$ .
Li .....	5.93	5.85 per cent.
$C_4H_4O_8$ .....	75.12	75.31     „

### *Rubidium Salt.*

A specially pure specimen of rubidium carbonate (from Schuchardt) dissolved in a very small quantity of water was added, in rather over the calculated quantity, to a strong solution of dihydroxytartaric acid, both solutions being ice cold. The somewhat bulky, crystalline precipitate which separated almost immediately was collected and washed three or four times with ice cold water, using only the smallest quantities necessary, as the precipitate diminished considerably in amount during the washing, being evidently more soluble than any of the salts so far examined. It was pressed and air-dried for about 24 hours, as in the other cases.

I. 0.5376 gram required 36.7 c.c. of permanganate B.

II. 0.4265 gave 0.2834  $Rb_2SO_4$ .

	Found.	Calculated for $\text{Rb}_2\text{C}_4\text{H}_4\text{O}_8 + 3\text{H}_2\text{O}$ .
Rb.....	42.53	42.19 per cent.
$\text{C}_4\text{H}_4\text{O}_8$ .....	44.44	44.46     ,,
(taking Rb = 85.4).		

*Cæsium Salt.*

A specially pure commercial specimen of cæsium carbonate was employed for the preparation of this salt. Examined spectroscopically, it appeared to be practically free from rubidium and from potassium. On mixing its concentrated ice cold solution with one of dihydroxy-tartaric acid in the same manner as in the previous cases, keeping the cæsium carbonate in excess, only a slight turbidity was produced, probably due to traces of sodium, and no separation of salt occurred even on standing for some time at  $0^\circ$ ; on repeating the experiment, however, with saturated, or very nearly saturated, solutions of the two substances, a white, crystalline precipitate began to separate almost immediately. This was collected and very carefully washed with small quantities of ice cold water, drained, pressed, and air-dried as before.

0.2902 gram required 17.2 c.c. of permanganate B.

$\text{C}_4\text{H}_4\text{O}_8 = 38.58$  per cent.

The solubility was determined (see below) and was found to be much greater than that of the salts previously examined, so that it was considered advisable to ascertain whether the composition was altered by fractional precipitation. The preparation of the salt was therefore conducted exactly as in the previous case, but the first portion, about one-third, of the precipitate which separated was quickly filtered off, and the remainder collected separately. The latter gave the following results on analysis.

0.3011 gram required 17.35 c.c. of permanganate B.

0.3482 gave 0.2593  $\text{Cs}_2\text{SO}_4$ .

	Found.	Calculated for $\text{Cs}_2\text{C}_4\text{H}_4\text{O}_8 + 2\text{H}_2\text{O}$ .
Cs .....	54.71	55.17 per cent.
$(\text{C}_4\text{H}_4\text{O}_8)$ .....	37.51	37.35     ,,

The *acid cæsium salt* appears to be less soluble, since it separates readily from moderately concentrated solutions when the acid is kept in excess. Only a small quantity of substance prepared in this way was available for examination. It was strongly acid to litmus.

0.4058 gram required 32.2 c.c. of permanganate B.

$\text{C}_4\text{H}_4\text{O}_8 = 56.47$  per cent.

Theory for  $\text{CsHC}_4\text{H}_4\text{O}_8 = 57.34$  per cent.

(taking Cs = 132.9).

*Acid Potassium Salt.*

A fairly concentrated ice cold solution of pure potassium carbonate (1·3 grams) was added to one of dihydroxytartaric acid (3·8 grams), the proportion of acid in excess of that calculated for the production of the acid salt (138 : 364).

The crystalline precipitate which separated was collected, washed, pressed, and air-dried as before. The aqueous solution of the substance is strongly acid to litmus. Analysis.

0·4656 gram required 53·5 c.c. of permanganate B.

0·4957 gave 0·1806  $K_2SO_4$ .

	Found.	Calculated for $KHC_4H_4O_8 + H_2O$ .
K .....	16·33	16·38 per cent.
$(C_4H_4O_8)$ .....	74·80	75·63 „

The solubility was determined in the same manner as in the cases previously mentioned, and was found to differ but slightly from that of the normal salt.

*Solubilities of the Dihydroxytartrates of the Alkali Metals.*

In the course of the experiments, previously recorded, on the quantitative estimation of sodium, it became a matter of some importance to determine the solubilities of the potassium, sodium, and ammonium salts at  $0^\circ$ .

Mixtures of water with considerable excess of the salt were kept in melting ice, with frequent stirring for half an hour, as owing to the unstable character of aqueous solutions of dihydroxytartrates a longer period was not considered advisable; moreover, this was the usual duration of the precipitation period in the quantitative estimations. The values must be regarded, therefore, rather as relative than absolute. At the expiration of this time, the mixtures were filtered, using a cold funnel, the first few drops being discarded, the solutions weighed in stoppered bottles, and the amounts of salt estimated by titration with permanganate.

The solubilities of the lithium, rubidium, and caesium salts were subsequently determined in exactly the same way. In all cases, the air-dried salt, as analysed, was used for the determination.

*Sodium Salt.*—Owing to the very sparing solubility of this salt, the permanganate solution (A) used for titration was diluted to 1/10.

4·24 grams of a saturated solution required 1·9 c.c. of permanganate (A/10) = 0·00168 gram  $Na_2C_4H_4O_8 + 3H_2O$ ; solubility = 0·039 in 100 parts.

*Potassium Salt.*—5.71 grams of a saturated solution required 16.8 c.c. of permanganate (A) = 0.1480 gram  $K_2C_4H_4O_8 + H_2O$ ; solubility = 2.66.

*Ammonium Salt.*—3.33 grams of a saturated solution required 11.4 c.c. of permanganate (A) = 0.0919 gram  $(NH_4)_2C_4H_4O_8 + 2H_2O$ ; solubility = 2.83.

*Lithium Salt.*—6.01 grams of a saturated solution required 0.55 c.c. of permanganate (B) = 0.0047 gram  $Li_2C_4H_4O_8 + 2\frac{1}{2}H_2O$ ; solubility = 0.079.

*Rubidium Salt.*—3.18 grams of a saturated solution required 13.3 c.c. of permanganate (B) = 0.1948 gram  $Rb_2C_4H_4O_8 + 3H_2O$ ; solubility = 6.51.

*Cesium Salt.*—1.48 grams of a saturated solution required 15.7 c.c. of permanganate (B) = 0.2724 gram  $Cs_2C_4H_4O_8 + 2H_2O$ ; solubility = 22.5.

*Acid Potassium Salt.*—2.21 grams of a saturated solution required 6.7 c.c. of permanganate (B) = 0.0583 gram  $KHC_4H_4O_8 + H_2O$ ; solubility = 2.70.

The solubilities of the dihydroxytartrates of the alkali metals are, therefore, greater as the atomic weight increases, lithium being the exception. The numbers are in the following ratio.

$$Li : Na : K : Rb : Cs :: 2 : 1 : 66 : 166 : 576.$$

It is probable, therefore, that this difference may be of service in separating the metals of the alkalis.

#### *Reactions of Soluble Dihydroxytartrates.*

The normal salts, when dissolved in ice cold water, give solutions which are neutral to litmus, but after standing for a short time at the ordinary temperature, a wine-red colour is developed owing to the decomposition into tartronate and carbon dioxide. This behaviour was to be expected from the results obtained on titrating the free acid by alkalis (*loc. cit.*, 74).

The following observations were made with ice cold and concentrated solutions of potassium dihydroxytartrate and various metallic salts.

*Silver nitrate* gives a white precipitate which soon darkens.

*Mercurous nitrate* gives a white precipitate which is not further reduced in the cold, but which immediately blackens on heating.

*Lead acetate* gives a white precipitate, and

*Mercuric chloride* is quickly reduced to calomel.

*Cupric sulphate* gives no precipitate, but the solution quickly turns green, and, on standing for some time, a fine, red deposit appears, consisting apparently of metallic copper.

*Fehling's solution* is reduced on heating.

*Barium* and *strontium* salts give bulky, white precipitates, and *Calcium chloride* produces a colourless, transparent jelly resembling hydrated silica in appearance.

No precipitate is produced by the following salts: *stannic*, *ferrous*, *ferric*, *aluminium*, *manganous*, *nickel*, *cobalt*, *zinc*, *magnesium*.

*Cadmium chloride* gives a slight, crystalline precipitate on standing.

*Chromic chloride* gives a transparent, green jelly

*Stannous chloride* produces a white, bulky precipitate, but if the dihydroxytartrate be in excess and the mixture gently heated, the solution shows, on testing with alkali and ferric chloride, a strongly marked reaction of dihydroxymaleic acid.

A similar reduction is effected by ferrous sulphate, and the ferric salt produced is sufficient to give the violet colour on the addition of alkali.

Dihydroxytartaric acid, although acting, therefore, as a powerful *reducing agent* towards silver, mercury and copper salts, is *itself reduced* by stannous or ferrous salts (also by hydrogen sulphide, hydrogen bromide, &c.).

#### *Barium Salt.*

With the object of preparing this salt, Barth (*Sitz. Acad. Wien.*, 82, ii, 1024) dissolved the sodium salt in dilute hydrochloric acid at 0°, and neutralised with baryta water; the numbers he obtained on analysing the precipitate indicated the formula  $\text{Ba}_3(\text{C}_4\text{HO}_7)_2 + 3\text{H}_2\text{O}$ , and the substance was regarded as the normal salt of tribasic 'carboxy-tartronic acid.' His preparation, however, was *dried at 100°* so that, from what has been stated as to the instability of the salts, it appears to be impossible that the substance analysed can have been dihydroxytartrate.

The following methods of preparation were now tried.

1. Precipitation of the free acid by excess of baryta water, taking great precautions to exclude carbon dioxide.
2. Precipitation of the free acid by excess of barium acetate.
3. Precipitation of the potassium salt with barium chloride.

In all cases, the solutions were kept in ice before mixing, and the precipitate was filtered through a funnel surrounded by ice, and washed with ice cold water.

The results obtained on analysing these precipitates varied considerably (Ba = 45—54 per cent.), and the products, whether air-dried or dried in a vacuum, effervesced when treated with dilute sulphuric acid in the cold. A certain amount of decomposition appears to take place during the process of drying, and this perhaps is to be expected, owing to the very bulky, almost gelatinous, nature of the precipitate.



Thorough draining from attached water is extremely difficult, even with a powerful pump, and traces of water would of course tend to decompose the salt at the ordinary temperature. (In the case of all the other dihydroxytartrates analysed, the precipitates are highly crystalline, and can be washed and drained with great rapidity.) Attempts were made to overcome this difficulty by repeatedly treating the washed precipitate first with alcohol and then with anhydrous ether, draining each time with the pump. This treatment had the effect of lowering the percentage of barium, and giving results better in agreement. Thus, a product prepared by method (2) and treated in this way gave Ba = 44.03, C = 14.37, H = 1.26. Another specimen prepared by method (3) gave Ba = 43.25. Both specimens were dried in a vacuum. These numbers approximate to those corresponding to the formula  $\text{BaC}_4\text{H}_4\text{O}_8$ , which requires Ba = 43.21, C = 15.14, H = 1.26.

But even these specimens showed some signs of effervescence when treated with dilute sulphuric acid, and, moreover, on titration with permanganate, the end point was very indefinite, and the results somewhat variable. Most probably, therefore, a portion had undergone decomposition into tartronate, carbonate, &c.

The *moist* precipitate, however, when first prepared, is acted on without any signs of effervescence by dilute sulphuric acid, and on titration with permanganate, gives sharp and definite readings, as in the case of other dihydroxytartrates. It was considered advisable, therefore, to determine the ratio Ba :  $\text{C}_4\text{H}_4\text{O}_8$  in the moist precipitate, since, bearing in mind the former differences of opinion as to the composition of the salt, it is evident that the value of this ratio is the matter of chief interest rather than the exact composition of the dry salt. According to Barth's formula, the ratio should be 3 : 2, whereas the present view would require the value 1 : 1, as was indicated in the experiments on titration of the free acid.

The moist precipitate was prepared by method (3), well washed with ice cold water, and drained for some minutes in a cold funnel as before. Two portions were then taken simultaneously and weighed as quickly as possible in closed vessels. The barium was then estimated in one portion by treatment with sulphuric acid, and dihydroxy-tartaric acid in the other portion by titration with permanganate.

I. 1.4720 substance gave 0.2321  $\text{BaSO}_4$ . Ba = 9.27 per cent.

II. 1.0120 grams required 22.15 c.c. of permanganate ( $\Delta$ )  
 $\text{C}_4\text{H}_4\text{O}_8$  = 12.56 per cent.

Therefore, Ba :  $\text{C}_4\text{H}_4\text{O}_8$  :: 1 : 1.02.

# LI.—*Affinity Constants of Dihydroxymaleic, Dihydroxyfumaric, Dihydroxytartaric, and Tartronic Acids.*

By SIDNEY SKINNER, M.A.

I AM indebted to Mr. H. J. H. Fenton for the very pure specimens of the acids used in the following measurements, the methods he employed for their preparation being described in his papers in the Society's Journal, 1894, 65, 899; 1895, 67, 48 and 774; 1896, 69, 546; and 1898, 73, 71. The measurements of electrical resistance were made by Kohlrausch's method, as described in Ostwald's "Physico-Chemical Measurements," page 222 (English translation), with the single modification that the alternating current was obtained from the town electric lighting supply, using suitable transformation to reduce the 100 volts to 1 or 2 volts. The cell, filled with distilled water, gave a resistance of some 40,000 ohms, and as the impurities in the distilled water were probably of a basic nature, no correction has been applied for the water, the acids being regarded as relatively strong (Ostwald, *loc. cit.*, page 235). In the tables

$\mu_v$  = molecular conductivity of the solution in mercury units.

$m$  = the fraction of the whole number of molecules ionised.

$k$  = the affinity constant calculated from the formula  $k = \frac{m^2}{(1-m)v}$ .

$v$  = the volume in litres which contains one gram-molecule.

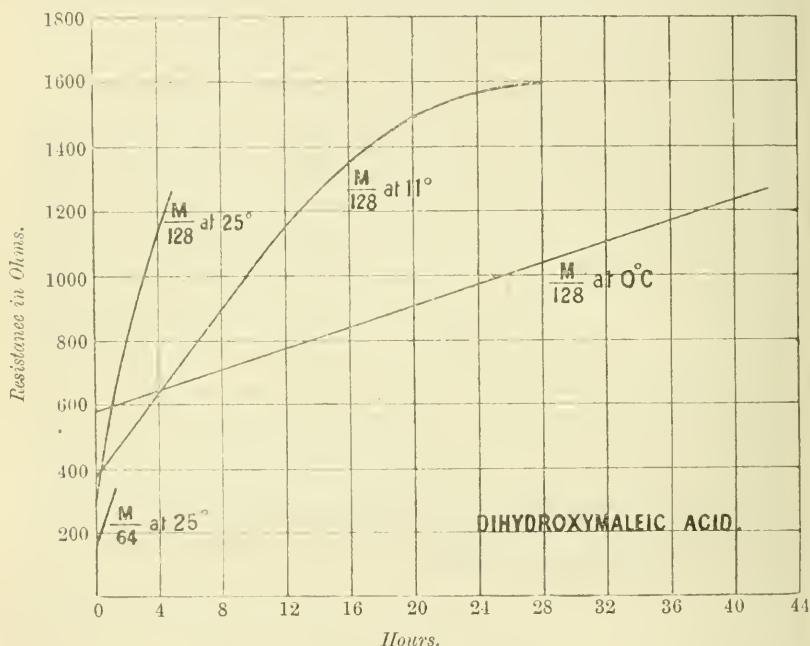
$K = 100k$  is given for comparison with the standard values of the affinity constant for other acids.

## *Dihydroxymaleic Acid.*

The determination of the affinity constant of this acid by means of measurements of electrical conductivity at 25° C. presents very considerable difficulty, as the acid decomposes rapidly in aqueous solution at this temperature. The use of a lower temperature is not permissible, as the constant could not then be compared with that of other acids, which have up to the present been examined only at 25°. If, however, the law which determines the change of conductivity with time could be ascertained, it was hoped that it would be possible to calculate the conductivity at the moment when the solution was made, and so eliminate the effect of decomposition. This has been done successfully, as it happened that the law at the commencement of the change was quite simple.

The acid in aqueous solution changes into carbon dioxide and glycollic aldehyde. The solution of glycollic aldehyde has low conducting power, and so the resistance of the acid solution increases with time. A number of measurements were made with a solution of the strength, one gram-molecule in 128 litres, at the temperatures  $0^{\circ}$ ,  $11^{\circ}$ , and  $25^{\circ}$ ; the results are given in tables I, II, and III, and are also shown in the accompanying diagram. This diagram shows

FIG. 1.



that, at  $0^{\circ}$ , the resistance for over 40 hours increased linearly with the time; at  $11^{\circ}$ , the variation of resistance with time was linear for about 10 hours, and then the resistance increased more slowly; at  $25^{\circ}$ , the variation was linear for 2 hours, and then it showed a similar falling-off as at  $11^{\circ}$ . In each case, some of the solution was boiled for 1 or 2 minutes so as to effect an almost complete change to glycollic aldehyde. The solution after boiling always gave a very high value of resistance.

From the fact that the change was at first linear, it was easy to determine the value of the resistance at the time when the solution was made; and these values have enabled me to calculate the affinity constant on the assumption that the acid gives at first the two ions,

H and  $\text{COOH} \cdot [\text{C} \cdot \text{OH}]_2 \cdot \text{COO}$ . Table V contains the values for two dilutions, that is, 184 grams in 64 litres and in 128 litres. The affinity constant has a mean value of 7.2, which is high for an organic acid, being near that of oxalic, which has the constant 10 (Ostwald, *Zeit. physik. Chem.*, 1889, 3, 281). Too much stress must not be laid on this value, as the acid is very highly ionised, namely, 84 and 91 per cent. for these dilutions, and it is probable that it is partly ionised to the three ions H, H and  $[\text{C}(\text{OH}) \cdot \text{COO}]_2$ . If this were the case, the affinity<sub>2</sub> constant should be calculated from the formula  $\frac{m^3}{(m-1)v^2}$ , which applies to triple ionised acids.

TABLE I.

M/128 at 0°.	Resistance in Legal	M/128 at 0°.	Resistance in Legal
Minutes from making solution.	ohms.	Minutes from making solution.	ohms.
10	573	110	606
19.5	587	*1365	936
33	589	1397	957
50	594	2525	1244
53	601	Solution boiled	4000
89	604	and cooled.	

TABLE II.

M/128 at 11°.	Resistance in Legal	M/128 at 11°.	Resistance in Legal
Minutes from making solution.	ohms.	Minutes from making solution.	ohms.
9	382	232	623
10	384	*236	623
14	390	274	671
18	394	317	687
33	411	1405	1564
56	433	*1413	1551
70	445	Solution boiled	2440
208	584	and cooled.	

\* At these points, fresh samples of solution which had been preserved at the respective temperatures in the stock flask were introduced into the resistance cell. This was done in order to determine whether the platinised electrodes by their presence were causing any decomposition of the acid.

TABLE III.

M/128 at 25°.	Resistance in Legal	M/128 at 25°.	Resistance in Legal
Minutes after making solution.	ohms.	Minutes after making solution	ohms.
6	322	75	600
12	338	81	634
15	350	88.5	664
16	351	98	707
20	368	108	753
29	403	118	791
34.5	423	*121.5	806
38.5	442	187.0	994
45.5	472	290.0	1252
55	511	Solution boiled	3000
65.5	562	and cooled.	

TABLE IV.

M/64 at 25°.	Resistance in Legal	M/64 at 25°.	Resistance in Legal
Minutes after making solution.	ohms.	Minutes after making solution.	ohms.
13	196	33.5	242
17	204	40	257
22	216	45	269
27	227	56	296

These numbers plotted on squared paper, give 165.2 ohms as the resistance of the solution at the moment the solution was made.

TABLE V.

Dihydroxymaleic acid,  $[C(OH) \cdot COOH]_2 + 2H_2O = 184$ .

Temperature 25°.

Dilution.	$\mu_v$	$m$	$k$
M/64	298.4	0.838	0.0694
M/128	325	0.913	0.075

For calculating  $m = \frac{\mu_v}{\mu_\infty}$ ,  $\mu_\infty$  has been taken as 356.

Probable value of  $K = 7.2$ .

The initial linear variation of resistance with time presents an interesting problem in chemical kinetics. The solid crystallised acid is quite stable at ordinary temperatures, but in aqueous solution it changes at 0° slowly, at 25° rapidly, into glycollic aldehyde and carbon

\* See Footnote, p. 485.



dioxide. The acid, when heated at 90—100° in a rapid current of hydrogen, loses its water of crystallisation, and the anhydrous acid is stable at this temperature. The anhydrous acid forms fairly stable solutions in alcohol and hot acetic acid; it may also be heated under boiling benzene without decomposition, but the addition of a small quantity of water causes the immediate evolution of carbon dioxide. From these facts, it appears that the action of water induces an instability, and regarding this action as an ionising one, it may be that the negative ion is the decomposing unit, and not the molecule of the acid. Taking this point of view, we must consider how the resistance of the solution would change if one of the ions were breaking up into a gas and a non-electrolyte (glycollic aldehyde). At first in solution the ions are certainly two, that is,  $\text{COOH} \cdot (\text{OH})\text{C}:\text{C}(\text{OH})\text{COO}$  and  $\text{H}$ . Let  $y_{\text{neg}}$  and  $y_{\text{pos}}$  be the concentrations of these ions;\* and if we attribute to the positive hydrogen ion a catalytic action as it has in the case of the inversion of cane-sugar by strong acids, then

$$-\frac{\Delta y_{\text{neg}}}{\Delta t} = c y_{\text{neg}} \times y_{\text{pos}}$$

where  $c$  is a constant and  $t$  the time, and since, there exists an equal number of positive and negative ions, we may write

$$-\frac{\Delta y}{\Delta t} = c y^2.$$

By integration,

$$\frac{1}{y} = \text{constant} + ct. \quad (1).$$

The conductivity of the cell at any moment is proportional to the degree of ionisation, so that

$$\mu \text{ varies as } \frac{1}{R} \text{ and as } y$$

or

$$\frac{1}{\mu} \propto R \propto \frac{1}{y}. \quad (2).$$

Therefore from (1) and (2)  $R \propto \frac{1}{y} \propto \text{a constant} + ct$ .

That is, the resistance must increase linearly with the time, which has been observed for the stronger solutions. In the more dilute solutions, at the later stages of the reaction, the law will no longer hold, for then we are probably dealing with three ions.

This explanation is not the only one which will give a linear result; one based on the view that the un-ionised portion of the acid is that

\* In the case of this acid, the ionisation is nearly complete (92 per cent.) for a solution of the strength 1 mol. in 123 litres.

which undergoes decomposition leads to a similar conclusion so long as only two ions are formed. Again, certain reactions of the acid indicate that hypothetical trihydroxysuccinic acid is formed at first, and that this breaks up into carbon dioxide and glycollic aldehyde.

(2) *Dihydroxyfumaric acid*,  $C_4H_4O_6 + 2H_2O$ .

$\beta$ -Modification, (Fenton, Trans., 1896, 69, 560).

M/64 at 25.2°, 0.2875 gram in 100 c.c.

Minutes after making solution.	Resistance in Legal ohms.	Minutes after making solution.	Resistance in Legal ohms.
15	201.6	31	230.6
16	201.2	36	241.6
18.5	203.6	42	255.6
21	209.8	46	265.2
26	219.2	51	276.2

Plotted on squared paper, these results give 161.0 ohms for the resistance of the cell at the moment the solution was made.

Dilution.	$\mu_v$ .	$m$ .	$k$ .
M/64	306	0.860	0.082.

For calculating  $k$ ,  $\mu_\infty$  has been taken as 356. The value of  $K = 100k$  is 8.2, a number slightly larger than that for dihydroxymaleic acid, which is 7.2. Only sufficient acid for a single solution was available, and the specimen was slightly coloured. Not so much weight can be given to this value as that of 7.2 for the maleinoid form, and perhaps the best conclusion is to regard both acids as having the same value for  $K$ .

*Dihydroxytartaric Acid*,  $\begin{array}{c} C(OH)_2 \cdot COOH \\ | \\ C(OH)_2 \cdot COOH \end{array} = 182$ .

0.5688 gram dissolved in 50 c.c. solution, M/16, at 10 hr. 47 m.  
Temperature 25°.

Time.	Dilution.	$\mu_v$ .	$m$ .	$k$ .
11 hr. 6 m.	M/16	126.7	0.358	0.0124
11 hr. 24 m.	M/32	162	0.458	0.0121
11 hr. 40 m.	M/64	198	0.557	0.0109
11 hr. 56 m.	M/128	233	0.659	0.0100
12 hr. 17 m.	M/256	267	0.754	0.00902
12 hr. 37 m.	M/512	293	0.830	0.00791
12 hr. 49 m.	M/1024	322	0.909	0.0088

For calculating  $m = \mu_v / \mu_\infty$ ,  $\mu_\infty$  has been taken as 354.  
Probable value of  $K = 1.24$ .

This acid, in aqueous solution, decomposes slowly into tartronic acid and carbon dioxide, and in order to determine how far the above results were vitiated by this change, a solution of dihydroxytartaric acid was made, M/32, and its resistance, measured at 25°, was 154 ohms, 62 minutes later it was 175 ohms, so that in 1 hour it had changed about 12 per cent. The value of  $K$  for tartronic acid given in the following section is 0·5. This slow change of the dihydroxytartaric acid must, therefore, result in a decrease in the value of its apparent  $K$  with time, and this is what has been observed. The value of  $K$ , obtained as soon as possible after making the solution, must, therefore, be taken as the most probable value for this acid.

*Tartronic acid*,  $\text{CH}(\text{OH})(\text{COOH})_2 = 120$ .

$\mu_x = 358$ . Temperature 25°.

Dilution.	$\mu_x$ .	$m$ .	$k$ .
M/11·08	74·8	0·209	0·00502
M/22·16	101·8	0·284	0·00510
M/44·32	132·0	0·3688	0·00487
M/88·64	167·5	0·468	0·00464

$K = 0\cdot5$ .

This acid was examined partly because a knowledge of its constant was necessary for the discussion of the constant of the previous acid, and partly because Ostwald had assigned to it a constant smaller than that of malonic acid, of which it is regarded as the monhydroxyl derivative. The value for malonic acid given by the same author is 0·158; and the value 0·5, given above, is greater, as it should be, according to theory. The reaction by which the sample of acid was prepared, namely, by heating in a water bath a strong solution of dihydroxytartaric acid, is so direct that it seems probable the sample of acid used by Ostwald contained some impurity. The melting point of the acid was 158—159°.

The following table gives the newly determined constants and those of the nearly related acids taken from Ostwald's list (*Zeit. physik. Chem.*, 188, 3, 418).

Malonic acid, 0·158	Succinic acid, 0·00665	{	Fumaric acid, 0·093
Tartronic acid, 0·5	Malic acid, 0·0395		Maleic acid, 1·17
	Dextro-and lævo-tartaric acids, 0·097	{	Dihydroxyfumaric acid, (7·2)
	Dihydroxytartaric acid, 1·24		Dihydroxymaleic acid, 7·2

The table shows.

1. The gradual increase of the constant on the introduction of hydroxyl groups.
2. The greater value of the constant for the lower members of the dibasic acids.
3. The greater value of the constant for the unsaturated acids in regard to their saturated homologues.

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## LII.—*Hydrolysis of Starch by Acids.*

By HAROLD JOHNSON.

It has been generally accepted that the hydrolysis of starch, due to acid conversion, is similar in character to that brought about by the action of diastase; except, of course, in that the maltose, the final product of the diastase conversion, is transformed by acids into dextrose. The products of the hydrolysis by acids, should, therefore, consist of amyloins (maltodextrins), maltose, dextrose, and perhaps an unreducing dextrin ( $C_{12}H_{20}O_{10}$ )<sub>n</sub>. Brown, Morris and Millar (Trans., 1896, 69, 121) evidently incline to this view, for they have shown that some fractions obtained by Lintner and Düll from conversions with dilute oxalic acid, after separation of the dextrose, would obey the laws of diastatic conversions, on the assumption that these fractions contained  $2\frac{1}{2}$  per cent. of moisture. However, Soxhlet (*Zeitschrift Spirit. Industrie*, 1884, No. 11) stated that the dextrins produced by the action of acids on starch were quite different from those produced by the action of diastase. Rolfe and Defren (*J. Amer. Chem. Soc.*, 1896, 18, 869), in "An Analytical Investigation of the Hydrolysis of Starch by Acids," found that starch when hydrolysed by dilute acids, even under varying conditions, obeyed certain laws. The fall in the specific rotation is constant throughout the action, and bears a certain relation to the cupric-reducing power, so that, given the one, the other may be calculated. Rolfe and Defren also stated that there are only three carbohydrates present at any time during the action, namely, maltose, dextrose, and dextrin, existing possibly in molecular aggregates; these authors calculated the relative quantities of maltose, dextrin, and dextrose present at any time of the conversion by means of curves, the percentage of these carbohydrates being represented by ordinates, and the specific rotatory powers as abscissæ in the same ordinate system. It is apparent from this communication that Rolfe and Defren also suppose the conversions by acids to be similar in character to conversions by diastase, except that, of course, as before stated, the

maltose of the diastase conversion is transformed by acids into dextrose.

The object of the present paper is to show that these conclusions are erroneous, and that the intermediate products of acid hydrolysis are not identical with those of diastase hydrolysis. These differences probably form the starting point of the controversies relative to starch hydrolysis which have arisen between the English and the German school; Brown and Morris\* maintain that the relation is constant between the cupric-reducing powers and specific rotations of the products of diastase hydrolysis, and can be expressed in terms of maltose and dextrin. Lintner and Düll have denied this relation, but as these authors (*Ber.*, 1895, 28, 1522) work indiscriminately on products from acid hydrolysis (after elimination of the dextrose), or from the products of diastase hydrolysis, it is not difficult to see how these differences may have arisen.

When the products of diastase conversions are fractionated by means of alcohol, the precipitated portions have specific rotations which may vary from about  $[\alpha]_{D^{35.6}} 150^\circ$  to about  $190^\circ$ . These fractions present the following peculiarities: they are unfermentable by Saaz yeast, and their cupric reducing powers and specific rotations can be expressed in terms of dextrin and maltose. Dextrin has a specific rotation of  $[\alpha]_{D^{35.6}} 195^\circ$ , and maltose  $[\alpha]_{D^{35.6}} 135.4^\circ$ , so that no substance resulting from diastase hydrolysis can have a special rotation of less than  $135.4^\circ$ . When, however, we separate fractions from the products of acid hydrolysis, the specific rotations vary between about  $[\alpha]_D 190^\circ$ , and  $[\alpha]_D 80^\circ$ . These fractions contain no free dextrose, because they are unfermentable by Saaz yeast; moreover, they cannot be molecular aggregates of maltose and dextrin, since the specific rotation of a maltodextrin cannot fall much below  $[\alpha]_D 150^\circ$ , and we are in presence here of fractions whose rotations can fall as low as  $80^\circ$ ; we have, therefore, intermediate substances present which do not exist in diastase conversions.

Before beginning an account of the work which follows, it is necessary to say a few words concerning the methods employed in the investigation. The directions given by Brown, Morris, and Millar (*Trans.*, 1897, 71, 72) were followed closely. The polarimeter used was a half-shade instrument, the readings being very accurate to  $0.1^\circ$ . As regards the determination of the cupric-reducing powers, at first the Soxhlet tube was used, the precipitated  $\text{Cu}_2\text{O}$  being reduced to metallic copper. However, a series of duplicate experiments, in which the  $\text{Cu}_2\text{O}$  was collected simply on a strong, double filter paper, and then dried and ignited in a platinum dish, showed that the latter

\* "Products of Starch Hydrolysis," Brown and Morris, *Trans.*, 1889, 55, 449—462; Brown, Morris and Millar, *Trans.*, 1897, 71, 73, 123.



method was the more accurate, and towards the end of the experiments this was alone used.

The Soxhlet tube presents the following inconveniences. The asbestos is extremely hygroscopic, holding water with the greatest tenacity, and even when dried in an oil bath at  $150^{\circ}$ , still retains water. This is a first cause of error; of course it may be reduced to a minimum by careful manipulation, but, when many determinations have to be made, it is impossible to devote all the time necessary to ensure accurate results. Secondly, the asbestos invariably loses weight during the collection of the  $\text{Cu}_2\text{O}$ , however carefully it may have been previously washed with acids and alkalis; perhaps this is due to the decomposition of the asbestos, or perhaps small portions of it are carried away in the washing. I had some tubes made expressly for me, with platinum cones fitting them exactly, but found that, however carefully the apparatus may be constructed, small difficulties will invariably present themselves. In dealing with the difficult problem of determining cupric-reducing powers, it is useless to complicate the apparatus; the simplest and most practical methods give the best results.

When the  $\text{Cu}_2\text{O}$  is collected on a filter paper, the following conditions must be observed to ensure accuracy. The filter with the precipitate, when completely washed, should be transferred to a wide, open platinum capsule, and dried in a water bath, the capsule being then heated over a low flame, preferably an argand burner, until the filter is completely burned, after which the contents of the dish are pounded with a small platinum pestle, which can be left in the capsule and weighed with it. The capsule is then placed over a Bunsen burner, heated to a dull red heat, and, when cold, the contents are again pounded. Finally, the capsule and contents are heated to a bright red heat, either over a very powerful Bunsen or in a muffle. The capsule is then cooled, and the contents weighed as  $\text{CuO}$ . The object of these manipulations is to ensure a thorough oxidation of the  $\text{Cu}_2\text{O}$ , which is incomplete if the heating is too vigorous at first.

If the two methods are carried out with all the care necessary, the results coincide very closely, but of the two the method of weighing as  $\text{CuO}$  is the simplest to perform, and open to less error than the process carried out in the Soxhlet tubes. It will be found impossible to wash the filter paper entirely free from the Fehling solution; this error should always be allowed for, and it differs with the kind of paper employed; the quantity was 0.003 gram for the paper which was used in these experiments. I have accepted as the cupric-reducing powers of dextrose the figures given by Brown, Morris and Millar (Trans., 1897, 71, 279); that these figures may be regarded as sufficiently accurate, is proved incidentally from the work which follows.

All values are expressed in terms of the factor 3.86 (for explanation see papers, Brown, Millar and Morris, already referred to). The specific rotation of soluble starch or dextrin has been taken as  $[\alpha]_{D3.86} 195^\circ$ , and that of dextrose as  $[\alpha]_{D3.86} 52.8^\circ$ . The starch was hydrolysed by means of dilute sulphuric or oxalic acid, and neutralised, after the conversion, respectively by barium or calcium carbonate; here there is another source of error which needs correction, and I have not anywhere observed that reference has been made to it. Barium and calcium carbonate are relatively very soluble in the saccharine solution resulting from the inversion, especially if the solution is fairly concentrated.

The calcium carbonate must be got rid of by careful precipitation with a weak solution of oxalic acid, and the barium carbonate by means of sulphuric acid. The solubility of these carbonates is in no way due to the presence of the carbonic acid resulting from the neutralisation of the acids, for after boiling a solution neutralised by barium carbonate, and leaving it for a week (of course, under aseptic conditions), a copious precipitate was produced on the addition of a few drops of sulphuric acid. In effecting this precipitation, it is, of course, necessary to carefully avoid the slightest excess of acid. The solubility of the calcium carbonate is even greater than that of barium carbonate, and leads to gross errors in the calculation of the solid matter, unless got rid of in the manner indicated. A pure starch is, of course, also necessary; this was obtained by washing good potato starch, first with 0.5 per cent. caustic soda to remove traces of proteid matter, and then with 3 per cent. HCl, finally washing with distilled water. The starch was saccharified at the boiling point of water, no pressure being exerted. The conversions were carried out in open beakers placed in a large water bath, the quantity of starch per 100 c.c. of water varying in the different trials from about 5 to 25 grams at the commencement of the hydrolysis, and the acid from about 3 to 8 grams per 100 c.c. As the beakers were not covered, the solutions became more concentrated as the hydrolysis proceeded, owing to the evaporation of the water, the solutions in some cases being reduced to one-half, or even one-third of their original volume; if any darkening of the solution was observed (this was the case when the sulphuric acid became too concentrated), a little distilled water was added. 50 to 80 grams of starch were taken for each experiment, and hydrolysed under varying degrees of concentration. Table A (p. 494) gives the results obtained from the hydrolysis of 16 different lots of starch.

The time taken for the hydrolysis varied according to the conditions of concentration and the point to which the hydrolysis was carried. A high percentage of starch retards the conversion, whilst a high percentage of acid has the opposite effect. As extremes for the times

taken to effect the conversions described in Table A, 12 minutes and 5 hours may be mentioned. The progress of the hydrolysis was followed by withdrawing the beaker from the water bath from time to time and determining the specific rotation of the solution. When the hydrolysis had reached the point desired, the acid was carefully eliminated, and the cupric-reducing power, the specific rotation, and the solids (by the factor 3.86) were carefully estimated.

Table A gives the results found for a series of conversions carried to different degrees. These results record the striking fact which seems to have escaped most observers up to the present, that the cupric-reducing powers and specific rotations of the products resulting from the action of acids on starch can be estimated in terms of dextrose and dextrin or soluble starch. (This is a verification of a statement made by M. Pellet (*Compt. rend.*, 2, 450) in a communication on commercial glucose read before the International Congress of Chemistry at Paris in 1896; M. Pellet, however, brought forward no experimental evidence to prove his assertion.) To render the results, as tabulated below, quite clear, a few explanations are necessary.

Column A gives the cupric-reducing power expressed as dextrose on 100 grams of 3.86 solids.

Column B, the dextrin by difference.

Column C, the specific rotation calculated from these percentages of dextrose and dextrin.

Column D gives the specific rotation found.

Column E, the difference between the specific rotation found and calculated.

TABLE A.

A.	B.	C.	D.	E.
13.90	86.10	175.2	174.4	+ 0.8
20.38	79.62	166.0	166.6	- 0.6
20.72	79.28	165.5	165.5	0
32.44	67.56	148.9	148.2	+ 0.7
33.70	66.30	147.1	147.7	- 0.6
40.03	59.97	138.1	137.9	+ 0.2
40.24	59.76	137.8	138.4	- 0.6
42.61	57.39	134.4	134.9	- 0.5
53.50	46.50	118.9	118.5	+ 0.4
57.55	42.45	113.1	112.6	+ 0.5
66.44	33.56	100.5	100.4	+ 0.1
70.18	29.82	95.2	95.4	- 0.2
79.14	20.86	82.4	81.9	- 0.5
80.43	19.57	80.6	80.3	+ 0.3
85.40	14.60	73.5	73.8	- 0.3
95.52	4.48	59.2	59.7	- 0.5

The figures of this table need little comment, being sufficiently striking in themselves. It will be seen that the differences between the specific rotations, found and calculated, do not exceed in any case more than  $0.8^\circ$ . If we take the mean of the differences, we find it only  $0.05^\circ$ , the *plus* differences and the *minus* differences being about equal; we can therefore consider them as errors of experiment.

Before proceeding farther, however, let us see what would be the error involved supposing there was a small amount of maltose present which had been calculated in terms of dextrose. Let us consider a case where we find in this manner 50 per cent. of dextrose and 50 per cent. of dextrin. The specific rotation of this conversion would be 123.9. Supposing 6.2 parts of the dextrose should be in reality calculated in terms of maltose, we should have 10 per cent. of maltose to substitute in its place; (maltose having a  $K$  of 62). We should then have a mixture containing 43.8 per cent. of dextrose, 10 per cent. of maltose, and 46.2 per cent. of dextrin, the specific rotation of which would be 126.75 in place of 123.9 as formerly. From this we see that, supposing there should be 10 per cent. of maltose present, and it has been estimated as dextrose, the rotation calculated would fall  $2.85^\circ$  short of the rotation found. An examination of the above table shows that the calculated rotation in no case falls below more than  $0.6^\circ$  that of the rotation found, and as we have pointed out, this small difference can be safely put down to experimental error. Rolfe and Defren (in the paper already referred to) asserted that a specific rotation of  $[\alpha]_D 129^\circ$  corresponded with the maximum percentage of maltose, namely, 44.1 per cent., the dextrin and the dextrose being present in equal quantities at this stage of the conversion. The conversion in the above table nearest to  $[\alpha] 129^\circ$  is one with a rotation of  $[\alpha] 134.9$ , and should contain about 40 per cent. of maltose according to Rolfe and Defren. If this were so, the rotation calculated as above would fall about  $11^\circ$  lower than that found. The rotations found and calculated agree, however, almost exactly, and, therefore, there can be no ground for the supposition that any maltose is present.

A number of fractions precipitated by alcohol from the products of acid conversion were next carefully examined. The cupric-reducing powers and specific rotations of these fractions, in a similar manner to the total products of conversion, can be expressed exactly in terms of dextrose and dextrin. These results are set out in Table B.

Column A contains the cupric-reducing powers expressed as dextrose on 100 grams of 3.86 solids.

Column B, the dextrin by difference.

Column C, the specific rotation calculated.

Column D, the specific rotation found.

Column E, fermentative action of Saaz yeast on the fraction.

Column F, Fermentative action of *Saccharomyces apiculatus*.



A.	B.	C.	D.	E.	F.
19.50	80.50	167.2	167.5	Nil.	Nil.
36.41	63.59	143.2	144.0	Nil.	Nil.
56.63	43.37	114.5	114.0	Nil.	Nil.
62.27	37.73	106.4	106.9	Nil.	Nil.
63.41	36.59	104.8	104.3	Nil.	Nil.
70.24	29.76	95.1	95.4	Nil.	Nil.
73.36	26.64	90.7	90.2	Nil.	Nil.
79.60	20.40	81.8	82.2	Nil.	Nil.

In order to show that these fractions were not merely mixtures of dextrose and other carbohydrates, they were put to ferment with Saaz yeast and *S. apiculatus*, some carefully prepared yeast water or a small portion of a nutrient solution containing asparagine and all the salts necessary for yeast development being added to afford nutriment for the yeast cells. All the necessary aseptic conditions were, of course, observed in carrying out these experiments. Nevertheless, as will be seen from Table B, these yeasts were quite powerless to set up the smallest fermentation. However, the type of yeast known as "logos," with which experiments were also made, produced a *partial* fermentation of the fractions, those with the lowest rotations yielding most readily to the action of this yeast.

Another proof that these fractions are definite compounds and not mixtures of dextrose and other carbohydrates is to be found in their behaviour when submitted to dialysis, the purified fractions, after being several times redissolved in water and again precipitated by alcohol, dialysing without undergoing material change in specific rotation. When a mixed fraction (that is to say, the precipitates resulting from a conversion thrown down by alcohol of increasing strength) is submitted to dialysis, the products that pass through the dialyser possess rotations lower than those of the substances remaining in the dialyser; however, the substances which pass through contain no free dextrose, as may be ascertained by putting them in presence of Saaz yeast, which will be found to fail to set up any fermentation.

The fractions, when submitted to a further treatment by acids, are completely transformed into dextrose, which is the final and only product of the conversion; the specific rotation remaining stationary at about  $[\alpha]_{D^{386}} 52^\circ$  to  $53^\circ$ , the dextrose is not affected by the acid, even when the concentration of the latter is as high as 15 per cent.

A point worthy of interest with regard to these fractions is the large range presented by their specific rotations, which vary from  $[\alpha]_{D^{386}} 80^\circ$  to  $[\alpha]_{D^{386}} 170^\circ$ . No attempt has been made to separate fractions with rotations higher than  $170^\circ$ , since they present no interest here, but that it is possible to separate them with higher rotations is shown by Lintner (*Ber.*, 1895, 28, 1522). It will be observed that the



lowest rotation presented by a fraction was  $82.2$  ; this corresponds very closely with 20 per cent. of dextrin and 80 per cent. of dextrose. This fraction dialysed without change. A substance of the same composition was also obtained by fermenting a conversion with a rotation of  $[\alpha]_{D^{38.6}} 60^\circ$  with Saaz yeast. The residue, after fermentation, contained 79.80 per cent. of dextrose and 20.2 per cent. of dextrin, and was evidently identical in composition with the fraction obtained by precipitation with alcohol.

A further proof that the substances from starch conversion by acids intermediate between starch and dextrose are *not* identical with those produced by diastase, is to be found in their behaviour towards diastase or malt extract. Soxhlet, as already mentioned, stated that diastase had no action on the dextrins from acid conversion. A careful examination has shown, however, that diastase *does* possess a slight action, but that, even on high conversions, its degrading power is very limited. This will be apparent on looking at Table C, where the results obtained by the action of malt extract on a number of conversions are tabulated.

Column A gives original rotation of the conversion.

Column B, the rotation after one hour's digestion with malt extract.

Column C, the rotation after two hours' digestion.

Column E, the fall in rotation.

The malt extract, obtained by digesting malt at  $30^\circ$  with distilled water, was added in quantities varying from 10 to 25 c.c. to each 10 grams of solids. The temperature employed was  $60^\circ$ .

TABLE C.

A.	B.	C.	E.
177.5°	165.9°	165.4°	12.1°
166.6	159.8	159.4	7.2
147.0	142.1	142.1	4.9
138.4	134.6	134.6	3.8
134.1	127.8	127.8	6.3
112.6	112.4	112.4	0.2
94.5	94.5	94.5	0

FRACTIONS FROM ALCOHOL.

A.	B.	C.	E.
167.5°	158.8°	158.8°	8.7°
144.0	142.8	142.8	1.2
114.0	114.0	114.0	0
95.4	95.4	95.4	0
82.2	82.2	82.2	0

It is rather difficult to account for this slight action which diastase has on the products of starch conversion by acids. The explanation that seems the most feasible is that the diastase attacks only the starch which has not been touched by the acid. As a rule the last traces of the blue colour\* produced by iodine do not disappear until the specific rotation has fallen to about  $[\alpha]_D 140^\circ$  or even lower. The point at which the blue coloration disappears depends a good deal on the concentrations of the acid and the starch; when the latter exists in concentrations of about 25 per cent. and the acid is very dilute (2 per cent.) a blue coloration will still be produced with iodine at a rotation of  $[\alpha]_D 115^\circ$ . The stronger the acid, the more quickly does the blue coloration disappear, thus, with a solution of starch at 5 per cent. and acid at 12 per cent., the blue coloration will disappear at a rotation of  $[\alpha]_D 150^\circ$ .

However, it must be stated that diastase has a slight action on conversions which give no blue coloration with iodine; perhaps in the splitting up of the molecule of starch there may be produced, as Brown and Morris have suggested, an unreducing dextrin,  $(C_{12}H_{20}O_{10})_n$ ; the slight fall in the rotation under the influence of diastase would then be due to degradation of this dextrin. It is, however, impossible to say anything for certain, except that diastase does possess a slight action on the products of starch hydrolysis by acids. It will be noticed that diastase has no action on fractions with rotations of  $114^\circ$  and lower; this is another proof that these are not mixtures of dextrose and amyloins.

From the above data, we can now resume as follows the properties of the substances intermediate between starch and dextrose, produced by the action of dilute acids on starch; the specific rotations of these substances vary between  $[\alpha]_{D_{3.86}} 80^\circ$  and  $190^\circ$ ; their cupric-reducing powers and specific rotations can be expressed in values of dextrose and the amylin group  $(C_{12}H_{20}O_{10})_n$ . This relation is shown by the following equation, in which  $K_{3.86}$  = the cupric-reducing power in terms of dextrose on 100 parts of the substance, and  $[\alpha]_{D_{3.86}} X^\circ$  = specific rotation. Then, given one of these values, the other can be calculated.

$$[\alpha]_{D_{3.86}} X^\circ = 195 - \frac{195 - 52.8}{100} K_{3.86}$$

\* With regard to the various colours such as red, brown, &c., produced by iodine at varying stages of the conversion, the author finds that they are of no value whatever, being produced by an intimate mixture of starch with other substances. This may be shown by taking a drop of the mixture giving the cherry red colour with iodine, and leaving it to dry for 24 hours on a white porcelain tile; at the end of this time, the starch will have separated out in the form of a number of little blue specks and the rest of the mass will be yellow, the red colour having quite disappeared. A microscopical examination of a drop left to dry on a glass slide will render this phenomenon still more apparent.

(The values given in this equation, of course, hold good for the total products of conversion, as well as the intermediate compounds.)

On simplification of the equation, we have

$$[\alpha]_{D_{3.86}} X^{\circ} = 195^{\circ} - 1.422 K_{3.86}.$$

When further treated by acids, these substances are completely transformed into dextrose. When treated by diastase, they undergo a slight fall in rotation when this value is not lower than about  $[\alpha]_{D_{3.86}} 120^{\circ}$ . They are unfermentable by Saaz and *apiculatus* yeasts, being partially fermented by logos. On purification, they dialyse without change. A precipitate thrown down by alcohol contains a mixture of these substances, whose solubility in alcohol decreases in proportion as their specific rotations rise. It should also be added that, when treated with phenylhydrazine acetate, they yield gummy precipitates. These precipitates were not further examined, owing to the difficulty experienced in attempting their purification; moreover, phenylhydrazine, as the history of starch hydrolysis has shown, is not a reagent on which much reliance can be placed for isolating the divers products of conversion. It is thus apparent from their character that these intermediate compounds are molecular aggregates of dextrose and the amylin group,  $(C_{12}H_{20}O_{10})_n$ , and, therefore, the author ventures to call them glucoamylin, which name accurately describes their composition. Moreover, in starch conversion by acids, there is no ground for supposing that at any time during the reaction is there formation of maltose or amyloins (molecular aggregates of maltose and the amylin group,  $C_{12}H_{20}O_{10}$ ), the sole products of the hydrolysis being dextrose and glucoamylin.<sup>†</sup>

Glucoamylin with low rotations can be easily obtained by fermenting with Saaz yeast a commercial glucose or a conversion made in the laboratory whose rotation is about  $[\alpha]_{D_{3.86}} 60-70^{\circ}$ . The residue after fermentation will have a rotation of  $[\alpha]_{D_{3.86}} 80-90^{\circ}$ , and will consist of glucoamylin. The existence in commercial glucose of an unfermentable reducing substance with a rotation of about  $80^{\circ}$  to  $90^{\circ}$  has been known of for a long time, and has received the name of gallasin. If we examine the properties usually attributed to gallasin, we shall see that it is nothing but a mixture of glucoamylin. Thus according to the various authors, the specific rotation of gallasin varies from  $[\alpha]_{D_{3.86}} 80^{\circ}$  to  $100^{\circ}$ , its cupric-reducing power is equal to about half that of dextrose, it is insoluble in strong alcohol, and on treatment with dilute acids is transformed completely into dextrose. These characters clearly show that gallasin is composed of a mixture of glucoamylin, but up to the present its real nature has escaped observation.

On first consideration, it seems strange that the intermediate compounds produced by the action of acids on starch should differ in

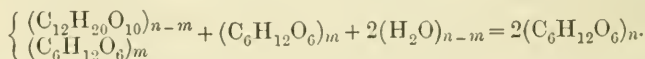
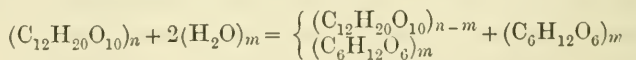
<sup>†</sup> The question of the existence of an unreducing dextrin,  $(C_{12}H_{20}O_{10})_n$ , is left aside.

character from those produced by diastase; however, on carefully looking into the matter we shall see that it is very easy to account for this difference. Dilute acids being able to hydrolyse free maltose, would also exercise this action on maltose combined in a molecular aggregate with the amylin group,  $(C_{12}H_{20}O_{10})_n$ , and therefore amyloins at the moment of their formation are transformed into glucoamylin and glucose (dextrose).

Maltose can be regarded as a simple anhydride of dextrose, being due to condensation of 2 molecules of the latter with loss of water. In the same way, starch may be regarded as an anhydride of maltose, being due to the condensation of at least 100 molecules of this carbohydrate, for, as Brown and Morris have shown, the molecular weight of soluble starch cannot be less than 32400,  $5(C_{12}H_{20}O_{10})_{20}$ . The anhydrous group in the amylin aggregates cannot, however, have the same structure as the anhydrous group in the maltose molecule, because diastase is only capable of hydrolysing one of these groups, with production of maltose and amyloins, whereas dilute acids hydrolyse both with production of dextrose and glucoamylin. The aldehyde groups of maltose and dextrose are probably formed at the moment of the hydration of the amylin aggregates by intramolecular rearrangement. Whether or not a dextrin with the formula  $(C_{12}H_{20}O_{10})_n$  is formed in the splitting up of the starch molecule there is no evidence to show, excepting the fact that diastase has a slight action on the products of conversion whose specific rotations lie between  $[\alpha]_D$  135° and 115°, and which give no blue coloration with iodine.

As diastase has no action on the products of conversion whose rotations are less than 115°, the dextrin, if produced, does not offer much resistance to the hydrating action of acids, and must be modified at an early period of the reaction.

For the present, however, it will be better to leave aside the possible existence of an unreducing dextrin, and to consider the reaction in its simplest form, which can be expressed by the following equations.



As a  $\sigma\chi\eta\mu\alpha$  for the formula of starch, the following figure is suggested.





*Starch σχημα.*

As will be seen on looking at the figure, each amylin group (between the large brackets) is composed of two maltose molecules (separated by the dotted lines) each of the latter being composed of two dextrose molecules. To show the points where the dextrose molecules condense to maltose and the latter to amylin groups, the  $H_2O$  molecules are inclosed in brackets. As is seen, the two dextrose molecules condense in a secondary group ( $HC \cdot O \cdot \overline{H} \quad \overline{HO} \cdot | CH$ ), whilst the maltose molecules condense in the primary group ( $H_2C \cdot O \cdot \overline{H} \quad \overline{HO} \cdot | CH_2$ ), the former becoming  $HC \cdot O - CH$  and the latter  $H_2C \cdot O - CH_2$ . The two aldehyde groups of the original dextrose molecules condense in the amylin group as is shown above. This explains the non-reducing character of starch. According to the above *σχημα*, the molecular weight of starch can be any multiple of  $(C_6H_{10}O_5)_4$ .

This figure is only intended to convey, in a figurative manner, the probable nature of the starch molecule, and is suggested by the behaviour of starch when submitted to the action of diastase or dilute acids. No claim is made that this represents the absolute formula of starch. The question of the possible formulæ of the glucoamylins presents too many difficulties to be dealt with here; however, I hope to return to it in a subsequent communication to the Society.

### LIII.—*Determination of Molecular Weights— Modification of Landsberger's Boiling Point Method.*

By JAMES WALKER and JOHN S. LUMSDEN.

IN determining the boiling point of the solution of a non-volatile substance, that is, the temperature at which the solution is in equilibrium with the vapour of the solvent, attention must be paid to the following points. The vapour and the solution must be intimately mixed in order that a proper equilibrium may be established, regular boiling must be ensured, and the heat exchange with the environment must be reduced to a minimum, as otherwise the temperature observed is not the temperature of equilibrium. The first condition is easily secured, for the solution when boiling briskly is continually agitated, and is always in intimate contact with the bubbles of vapour passing upwards. The others are more troublesome. It is necessary in the first place to reduce the radiation and conduction towards the exterior to a minimum by jacketting the solution with the vapour of the

boiling solvent. In the second place, when the source of heat employed is of a temperature much above the boiling point to be measured, as is the case when the solution is boiled by an external flame alone, irregular boiling and superheating can only be avoided by the use of such devices as are given by Beckmann (*Zeit. physikal. Chem.*, 1889, 4, 543; 1891, 8, 223; 1894, 15, 656); Sakurai (*Trans.*, 1892, 61, 989) employs an external flame, but in addition passes the vapour of the solvent through the solution, thereby securing regular ebullition and thorough mixing.

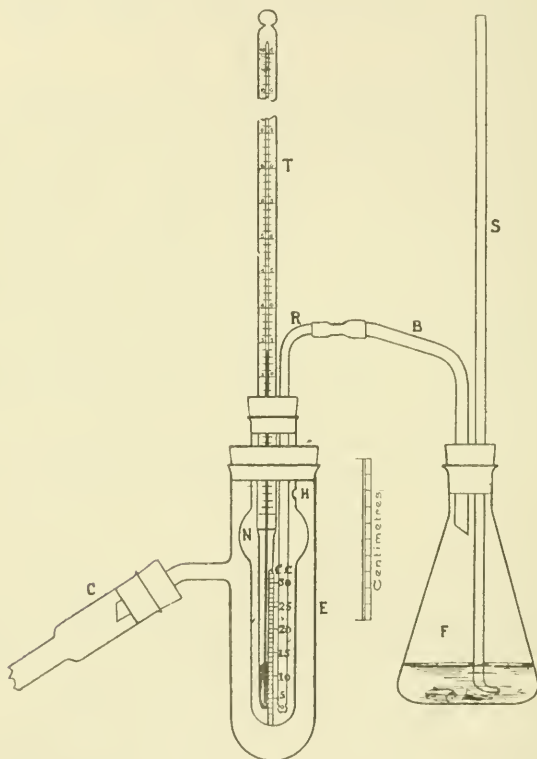
Landsberger has recently described (*Ber.*, 1898, 31, 458) a method adapted for the determination of the molecular weight of substances in solution, in which the external flame is discarded altogether, the solution being kept at its boiling point by the passage through it of the solvent vapour alone, so that superheating is entirely prevented. His method is extremely simple and rapid, and, as we can testify, yields very satisfactory results. In this paper, we describe a slight modification of his apparatus, by means of which a further saving of time is effected, and several successive readings with the same portion of dissolved substance are rendered possible, the error not exceeding that of a Victor Meyer vapour density determination. The method we propose is adapted to obtaining values easily and rapidly in the course of ordinary organic or inorganic research work, and not to obtaining accurate values for physico-chemical purposes.

The modification consists in reading the *volume* of the solution after equilibrium has been attained, instead of ascertaining its *weight*. It is usual to calculate the molecular weight of a substance in solution by expressing the strength of the solution in grams per 100 grams of solvent; Arrhenius pointed out, however, that it was equally feasible to calculate the molecular weight of dissolved substances by expressing the strength of the solution in grams per 100 cubic centimetres. Arrhenius' method gives lower results for the molecular weight than the other, but the difference between the two is only great in strong solutions. The theory on which the calculation of molecular weights by the boiling point method is based holds good for dilute solutions only, and affords no clue as to which mode of calculation should be preferred when the solutions are concentrated. It is therefore a matter for our convenience which of the two we select; and Beckmann has shown that in some cases the one method gives numbers more in accordance with the molecular weight corresponding with the usual chemical formula, and in some cases the other. The only difference in the actual calculation is that a different constant has to be employed for each solvent when volumes are measured instead of weights.

The apparatus we have used is shown in the accompanying figure.

It consists of the flask F, the inner tube N, which contains the solution, and the outer tube E, which is connected with the condenser. The vapour is generated in F, passes through the solution in N, from which it issues through the hole H, to form a vapour jacket between the two tubes, and finally passes into the condenser. We find it expedient

FIG. 1.



to have the tube B 6—7 mm. in bore, bent obtusely, as shown in the figure, and drawn out so as to be connected with R by a piece of rubber tubing. The lower end of R, where the vapour passes into the solution, is perforated with a rose of four horizontal holes and one terminal hole. The bubbles of vapour are by this means better distributed through the liquid than when the tube is cut off square, and there is less tendency to excessive frothing. The inner tube, which is graduated in cubic centimetres up to 30 c.c., is provided with a bulb above the highest graduation; this bulb prevents portions of the solution being projected through H when the amount of liquid in the tube is great and the boiling vigorous.

The mode of conducting an experiment is as follows: First, the boiling point of the solvent is determined. This is done by placing about 12 c.c. of the liquid in the boiling tube N, and passing the vapour generated in the flask through it until drops fall from the condenser at the rate of, at least, one every two seconds; the thermometer is then read and the boiling interrupted. The thermometer and the tube R are now removed, and the graduated tube transferred with its cork to an upright cylinder of just sufficient diameter to admit the graduated portion easily. This ensures that the tube is vertical, so that the volume of liquid in it may be read accurately. A knowledge of the volume of the solvent alone is not necessary for the calculation, but is of service in forming an estimate of the accuracy of the results.

The bulk of the liquid is next poured out of the tube so that only about 5—7 c.c. remains, then from half a gram to a gram of the substance to be investigated is added and the tube replaced in the apparatus. The vapour is again passed through the liquid until drops come from the condenser at the same rate as before; the thermometer is read and the boiling flask immediately after disconnected at R. If the solvent is inflammable, the flame beneath the flask should be previously extinguished or removed to a safe distance. The tube N is again disconnected, introduced into the upright cylinder, and the volume of liquid again ascertained. With as little delay as possible, the parts of the apparatus are replaced, vapour once more passed through it, and the determinations of the temperature and the volume of the solution repeated. This series of operations may go on until half a dozen determinations at different dilutions have been obtained, for at each successive reading not more than 2 or 3 c.c. of the solvent will have condensed in the solution.

The chief saving of time is effected by there being only a single weighing necessary for all the determinations, if the substance is in the form of a compressed pellet, or two if the weighing is made by difference. The reading of the volume is quite accurate enough, although the tube is only graduated in single cubic centimetres; for tenths of a c.c. can be easily estimated and the total volume to be read is not less than 10 c.c., so that the error from this source does not exceed 1 per cent. If the apparatus is once in working order, it is possible to make five or six determinations with the same quantity of substance in half an hour, although, as a rule, three will suffice for all practical purposes.

For calculating the molecular weight, use is made of the following formula, the weights being given in grams and the volumes in cubic centimetres.

$$\text{Mol. wt.} = \frac{\text{Constant} \times \text{Weight of substance}}{\text{Elevation} \times \text{Volume of solution}}$$

The constants for the various solvents are given in the subjoined table. They are equal to the ordinary constants divided by the specific gravity of the solvent at its boiling point (compare Beckmann, *Zeit. physikal. Chem.*, 1890, 6, 472.)

Alcohol .....	1560	Acetone .....	2220
Ether .....	3030	Chloroform .....	2600
Water .....	540	Benzene .....	3280

With regard to the practical carrying out of the process, several points have to be noted. It is necessary, as Landsberger states, to add a fresh piece of porous tile to the liquid in the boiling flask each time the flask is disconnected and the boiling interrupted. If this is not attended to, the boiling is irregular, and the results untrustworthy. The choice of a solvent is also a matter of considerable practical importance; when possible alcohol or ether should be used. Acetone, if pure, gives very good results, but that usually employed as a solvent is useless for repeated determinations, as the composition of the solvent changes as the distillation progresses. Benzene, water, and chloroform have all special disadvantages. Benzene, owing to the combination of comparatively high boiling point and small heat of vaporisation, condenses very rapidly within the apparatus, so that it is not possible (even when no liquid is introduced into the tube N from the beginning, and when the outer tube is protected by a non-conducting coat) to obtain more than two successive readings under favourable circumstances for accuracy. There is also the drawback in the case of benzene that it is a solvent in which the dissolved molecules have a great tendency to associate, with the result that the molecular weight thus determined is frequently double the molecular weight determined by the method of vapour density; this applies especially to compounds containing the hydroxyl group, and in their case benzene should never be used as solvent. Water is a solvent which for a given strength of solution gives a very small elevation of the boiling point, and is therefore to be discarded when ether or alcohol can be employed. The high specific gravity of chloroform renders it unsuitable for molecular weight determinations by the method above described. The bulb of the thermometer and the point at which the vapour enters the solution are at the lowest part of the tube N, and it is here that the temperature of equilibrium between vapour and solution is measured, but it is obvious that this temperature is not measured under exactly the same conditions in the successive readings at different volumes. When the volume is great, the pressure at the bottom of the tube N is greater than when the volume is small, and consequently the observed temperature is higher in the first case than in the second, even when the solvent alone is used;



moreover, the difference of pressure is greater as the liquid in the tube is denser, so that liquids of low specific gravity are to be preferred as solvents. It is to reduce the error from this source to a minimum that the boiling point of the solvent is determined with a considerable quantity of the liquid in the inner tube; the conditions are then the same as those for the most dilute solutions, that is, for those that show the smallest elevation of the boiling point. When the volume of the solution is small, the difference between its boiling point and that of the solvent is great, and an error on the difference has a comparatively small effect. If the boiling point were determined with only a small quantity of the solvent, the error would be greatest when the difference measured was least and would thus lead to a serious error in the molecular weight.

The thermometer used should have, as Landsberger recommends, a small bulb and as light a stem as possible. As the accuracy to be aimed at in actual laboratory determinations of molecular weights need not be great, it is unnecessary to have a thermometer graduated more finely than in tenths of a degree, indeed a thermometer graduated in fifths will serve most everyday purposes. If the scale of the thermometer is a good one, it is then easy by means of a lens to estimate fiftieths, or even hundredths, of a degree, and this degree of accuracy does not lead to an error of more than four or five per cent. at most in the molecular weight, since the elevation measured is not often less than half a degree, except in the case of water.

The following numbers were obtained with a thermometer graduated in fifths, and will give an idea of the accuracy of the method.

#### ACETONE AS SOLVENT.

0.829 gram *Camphor*. Mol. wt. 152.

Elevation.	Volume.	Mol. wt.
1.47	8.1 c.c.	154
1.09	10.7	159
0.71	16.7	155
0.64	19.0	151

0.662 gram *Resorcinol*. Mol. wt. 110.

1.77	8.7 c.c.	95
1.05	16.0	88
0.85	18.0	96

The number obtained by Landsberger for the molecular weight of resorcinol is 98 with acetone as solvent.

0.672 gram *Naphthalene*. Mol. wt. 128.

Elevation.	Volume.	Mol. wt
0.97	12.1 c.c.	128
0.67	17.8	126
0.52	24.6	117

0.512 gram *Benzoic acid*. Mol. wt. 122.

0.80	11.6 c.c.	123
0.54	16.8	126

#### CHLOROFORM AS SOLVENT.

0.552 gram *Naphthalene*. Mol. wt. 128.

1.20	9.5 c.c.	126
0.65	17.7	125

0.787 gram *Benzoic Acid*. Mol. wt. 122.

0.87	11.5 c.c.	208
0.55	17.8	209
0.45	23.5	193

There is here a considerable association of the simple molecules, as other observers have found with this solvent.

#### ETHER AS SOLVENT.

1.536 grams *Paratoluidine*. Mol. wt. 107.

3.75	11.2 c.c.	111
3.15	13.8	107
2.37	18.8	104
1.79	26.0	100
1.60	29.0	99

0.917 gram *Resorcinol*. Mol. wt. 110.

1.92	11.3 c.c.	128
1.27	19.0	115
1.17	21.4	111
0.90	28.0	111

0.558 gram *Benzoic acid*. Mol. wt. 122.

1.08	12.0 c.c.	130
0.85	15.0	133
0.66	20.8	123

## ALCOHOL AS SOLVENT.

1.057 grams *Naphthalene*. Mol. wt. 128.

Elevation.	Volume.	Mol. wt.
1.08	9.7 c.c.	157
0.75	15.0	147
0.55	19.4	154

Beckmann finds 148 and 155.

0.835 gram *Mercuric chloride*. Mol. wt. 271.

0.49	10.1 c.c.	263
0.32	15.6	261

Beckmann found 264, and Landsberger 275.

0.345 gram *Urea*. Mol. wt. 60.

0.83	9.4 c.c.	70
0.57	14.1	67
0.43	19.0	66

Landsberger found 65, Beckmann 63.

0.544 gram *Benzoic acid*. Mol. wt. 122.

0.71	9.8 c.c.	122
0.33	20.2	127

0.72 gram *Salicylic acid*. Mol. wt. 138.

0.84	9.7 c.c.	138
0.62	14.3	127
0.46	19.5	125

## WATER AS SOLVENT.

0.522 gram *Potassium nitrate*. Mol. wt. 101.

0.60	8.8 c.c.	53
0.40	13.3	53

0.718 gram *Sodium chloride*. Mol. wt. 58.5.

0.88	13.9 c.c.	32
0.72	17.0	32

In the case of these salts, the molecular weight is reduced to little more than half by electrolytic dissociation.

1.169 grams *Urea*. Mol. wt. 60.

1.24	8.1 c.c.	63
0.64	15.0	66

Landsberger found 62.6 and 65.4.

## BENZENE AS SOLVENT.

0.668 gram *Naphthalene*. Mol. wt. 128.

Elevation.	Volume.	Mol. wt.
1.40	11.3 c.c.	139
0.70	22.2	141

Landsberger found 144, and Beckmann 144.

0.487 gram *Anthracene*. Mol. wt. 178.

0.81	10.0 c.c.	197
0.53	16.0	188
0.41	21.2	184

Landsberger found 190, Beckmann 192.

0.911 gram *Benzoic acid*. Mol. wt. 122.

0.90	13.2 c.c.	252
0.57	23.4	224

Landsberger found 232, Beckmann 244.

We are indebted to Mr. W. A. Fyffe, who had no previous experience in the determinations of molecular weights by the boiling point method, for the following experiments.

1.33 grams *Potassium bromide* in *water* as solvent. Mol. wt. 119.

1.20	9.5 c.c.	63
0.98	11.5	63
0.88	13.5	60
0.82	15.0	58

1.04 grams *Phthalic anhydride* in *alcohol*. Mol. wt. 148.

1.50	7.0 c.c.	154
0.96	10.8	156
0.70	14.8	156
0.60	18.0	150

1.46 grams *Diphenylamine* in *alcohol*. Mol. wt. 169.

1.02	13.0 c.c.	172
0.80	16.5	172
0.72	19.0	167

1.46 grams *Diphenylamine* in *ether*. Mol. wt. 169.

2.72	9.3	175
2.42	10.5	174
2.20	11.8	171
1.82	14.5	168
1.80	15.3	161

These results are sufficient to indicate that, even by using a single thermometer with a scale reaching to  $102^{\circ}$ , and graduated in fifths of a degree, numbers for the molecular weights are rapidly obtained by this method, which are accurate enough for preparatory or research work in organic or inorganic chemistry. For such purposes, the more exact methods, indispensable for physico-chemical work, entail a complexity of apparatus, and an expenditure of time and trouble out of all proportion to the actual value of the accuracy attained. The points in which the above method differs from Landsberger's are, first, that a series of determinations can be made with the same quantity of material; and second, that only one weighing is necessary for the whole series, whereby a great saving of time is effected.

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#### LIV.—*Rate of Escape of Ammonia from Aqueous Solution.*

By EDGAR PHILIP PERMAN, D.Sc.

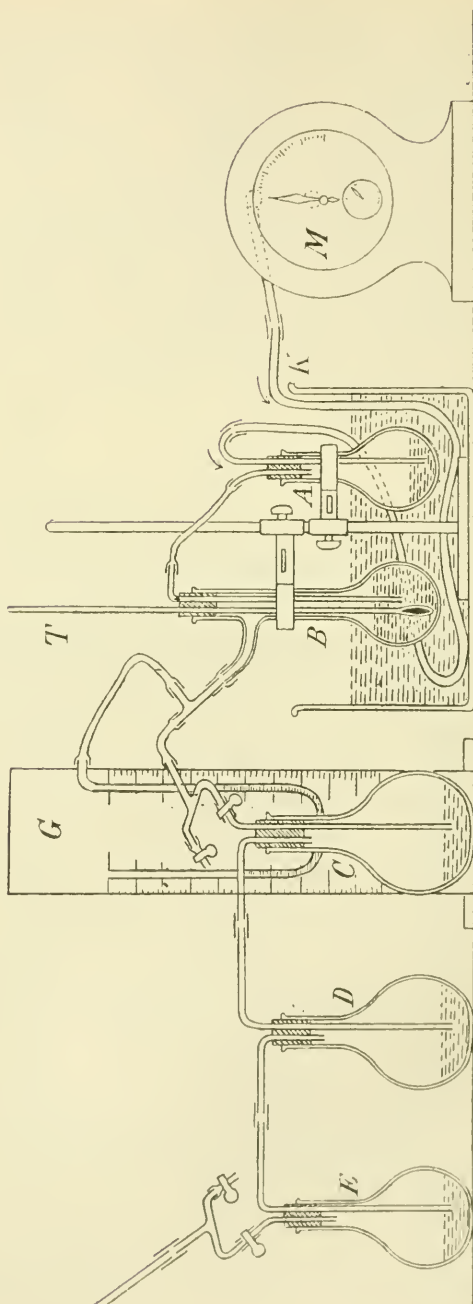
IN a recent paper on "Rate of Escape of Gases from Solutions of varying Concentration" (Trans., 1895, 67, pp. 868 and 983), the author has shown that, if a current of air is aspirated at a uniform rate through an aqueous solution of ammonia, the amount of ammonia in solution at any time  $t$  mins. from the beginning of aspiration is accurately represented by the equation  $\log q = a + bt$ , where  $q$  = amount of ammonia in solution;  $a$  and  $b$  are constants.

It was suggested by Mr. Vernon Harcourt that it would be better to measure the volume of air passing through the solution by means of a meter, instead of measuring the time of aspiration. A meter procured from Messrs. Alexander Wright and Co. was tested by aspirating measured volumes of air through it at varying rates, and also by forcing air through it. The results of these experiments proved the probable error of the meter to be less than 1 per cent.

Some experiments were then made to discover whether the formula  $\log q = a + bt$  could be replaced by  $\log q = a + bV$ ,  $V$  = vol. of air (in litres) aspirated through the solution. The apparatus was similar to that used in the previous research, except in the following particulars; two sets of absorption flasks were used, so that the air-current could be passed through either set by means of two T-pieces and four clips, Fig. 1, p. 512. A thermometer, T, divided to  $0.1^{\circ}$ , was fixed into the aspiration flask B by means of a cement of litharge and glycerol. The air passed first through the meter M, then through a lead pipe K, coiled



FIG. 1.



in the dish of water, to the first flask A, which contained water so as to saturate the air with aqueous vapour, and to make up for loss of water by evaporation in B. B contained the ammonia solution; its capacity was a little more than 50 c.c., thus leaving very little spare space, 50 c.c. being the amount of the solution always used. C contained a measured quantity of standard sulphuric acid solution, and D and E contained distilled water. Nearly the whole of the ammonia drawn off was absorbed by the acid in C, only traces were found in D and E, and the total amount of ammonia was ascertained to be equal to that taken at the beginning of the experiment.

As it was found that the thermometer fell  $0.5^{\circ}$  or more in a few minutes after beginning the aspiration, the first portion of ammonia was not estimated; as soon, however, as the temperature became constant, the air current was directed through the other set of flasks, and the ammonia absorbed was afterwards estimated. In some of the experiments, a barrel was used as an aspirator, but the water pump and the regulator were always used with a quick air current. The following numbers were obtained with a current of air of 1.130 litres per min.

Temp. of solution  $13.4^{\circ}$ .

<i>Vol. of air aspirated.*</i>	<i>NH<sub>3</sub> in solution (q).</i>	<i>Log q (observed).</i>	<i>Log q (cal.).</i>
0 litre	3.686 grams	0.5666	(0.5666)†
7	3.406	0.5322	0.5332
15	3.117	0.4937	0.4951
24	2.823	0.4507	0.4522
31	2.619	0.4181	0.4179
40	2.377	0.3760	(0.3760)
$a = 0.5666, b = -0.004765.$			

This was one of the quickest currents used, and the experiment was a difficult one, owing to the short time available for recharging the flasks with acid solution. The aspiration was continuous throughout the experiment; while the absorption of ammonia was going on in one set of flasks, the other set was being recharged.

These results show that the values of  $\log q$  are accurately given by the equation  $\log q = a + bV$  under the conditions of the experiment, or it may be written  $\log q = a - bV$ , when  $b$  becomes positive. The conditions were varied in several different ways in order to discover the relation between them and the rate of escape of the ammonia.

\* The volumes given are those read on the meter.

† The numbers in brackets were taken as data for finding the value of  $b$ , and from this the other values of  $\log q$  were calculated.

*Variation of Concentration.*

In order to obtain the greatest possible variation in the concentration of the ammonia solution, 50 c.c. of strong solution were taken, and the ammonia drawn off until only about 1 gram remained; although it was found impossible to keep the temperature very constant, owing to the rapid loss of heat caused by the evaporation of the ammonia, it was maintained as nearly as possible at 20° by adding hot water when necessary. The results obtained are here given.

*Concentrated Ammonia Solution.*

Temperature of solution, 19.9°. Bar., 766 m.m. Rate of air current, about 0.3 litre per minute. Temperature of air passing through the meter, 15°.

<i>Vol. of air aspirated.</i>	<i>NH<sub>3</sub> in solution (g)</i>	<i>Log q.</i>	<i>Δlog q/ΔV</i>
0 litres	14.207 grams	1.1525	0.0414
2	11.742	1.0697	0.0263
5.5	9.496	0.9775	0.0186
11.5	7.345	0.8660	0.0141
22	5.218	0.7175	0.01104
42	3.138	0.4966	0.00919
62	2.055	0.3128	0.00851
89	1.211	0.0831	

If the equation  $\log q = a - bV$  held for all concentrations of the solution, the values of  $\Delta \log q / \Delta V$  would be constant, but the value is seen to increase largely with the concentration. No simple formula has been found which will express the relation between  $q$  and  $V$  in the case of concentrated solutions. The experimental results are probably not very accurate, owing to the difficulty in keeping the temperature of the solution constant.

The ammonia solution used for further experiments contained about 70 grams of ammonia per litre at a temperature of 15°. No attempt was made to preserve the solution at *exactly* the same concentration, as small alterations make no difference in the value of  $b$  found from the experiments. It has already been shown that, with such a solution, more than 1 gram of ammonia may be removed without causing any discrepancy in the results calculated from the logarithmic formula, and this will be confirmed by many more results given later on.

*Variation in the Rate of Air-current.*

The two following experiments were carried out at a temperature of 13.4° with very different rates of air-current. The numbers calculated

from the logarithmic formula are seen to express well the experimental results.

Rate of air-current, 0.637 litre per minute. Temperature of ammonia solution, 13.4°. Pressure in aspiration flask, 758 mm.

<i>Vol. of air aspirated.</i>	<i>NH<sub>3</sub> in sol. (q).</i>	<i>log q (observed).</i>	<i>log q (cal.).</i>
0 litres	3.678 grams	0.5656	(0.5656)
6	3.439	0.5364	0.5368
12	3.217	0.5075	0.5081
18	3.010	0.4786	0.4793
24	2.819	0.4501	0.4506
30	2.641	0.4218	(0.4218)

Rate of air-current, 0.20 litre per min. Temp. of ammonia solution, 13.4°. Pressure in aspiration flask, 750 mm.

<i>Vol. of air aspirated.</i>	<i>NH<sub>3</sub> in sol. (q).</i>	<i>log q (observed).</i>	<i>log q (cal.).</i>
0 litres	3.649 grams	0.5622	(0.5622)
6.05	3.413	0.5331	0.5325
12.10	3.194	0.5043	0.5027
18.15	2.980	0.4742	0.4730
24.20	2.781	0.4442	0.4433
30.25	2.591	0.4135	(0.4135)

The rate of escape of the ammonia, when any definite amount  $q$  grams of ammonia is in solution, is found by differentiation of the expression  $\log q = a - bV$  to be  $bq$ ; that is, the amount of ammonia that would be removed by passing 1 litre of air through the solution, supposing the strength of the solution to remain constant, is  $bq$  grams;  $b$  is therefore a measure of the rate of escape of the gas from any solution as long as the logarithmic law holds good; it is, in fact, the amount of ammonia that would be drawn off by 1 litre of air, supposing the solution to always contain 1 gram of ammonia.

A number of experiments were carried out under conditions similar to those already described, and the process was simplified by making one continuous aspiration after the temperature of the solution had become constant;  $b$  was found at once from the expression  $b = (a - \log q) \div V$ ,  $a$  being the logarithm of the amount of ammonia in the solution when the aspiration commences, and  $q$  the amount at the end. The pressure of the gases in the aspiration flask was read by means of a pressure-gauge G, Fig. 1, (p. 512), combined with the reading of the barometer. The volume of air passed through the solution was in every case reduced to the pressure in the aspiration flask and the temperature of the solution before calculating the value of  $b$ . The air was assumed to become saturated with aqueous vapour on passing through the meter; that this is the case was proved by testing the

meter with air passing in from a dry room, and again with air saturated with aqueous vapour by bubbling through three flasks containing water. The results show no difference in the two cases.

<i>Barrel.</i>	<i>Meter.</i>
5 litres	4.97 litres, dry
5	4.99 „ saturated
5	4.93 „ dry
5	4.93 „ saturated

In calculating  $b$ , the volume read on the meter was corrected to the corresponding volume of *dry* air, and then reduced to the temperature and pressure of the solution. It may be said that the volume of air at its *partial pressure* in the aspiration flask should be reckoned; but the partial pressure is not constant, owing to the escape of the ammonia, and, moreover, if it could be calculated in that way, equal volumes read on the meter would not represent equal volumes in the aspiration flask, and the logarithmic equation would not hold at all. To take an example, the amount of ammonia drawn off by 20 litres of air in an experiment at  $20^{\circ}$  was 0.89 gram, which at the temperature of the solution would occupy as a gas a volume of 1.26 litres; this gives as the mean pressure of the ammonia present in the mixture of ammonia and air (neglecting the aqueous vapour)  $1.26/20 = 0.063$  atmosphere; the actual pressure of the ammonia will, however, decrease as the ammonia is drawn off, and will be roughly proportional to the strength of the solution, as shown by the experiments of Roscoe and Dittmar on the solubility of ammonia at different pressures. The strength of the ammonia solution varies about one-fourth; therefore, the pressure of the ammonia in the gaseous mixture will vary about  $0.063/4 = 0.016$  atmosphere, an amount which would affect the experimental results to a very appreciable extent. It would seem that the molecules of air only are effective in carrying off the ammonia. However this may be, the method of calculating the volumes adopted is the most convenient for obtaining comparable results under various conditions.

For the temperature,  $13.4^{\circ}$ , the following values of  $b$  were obtained; the experimental data are given in the Appendix (p. 526).

<i>Rate of air current.</i>	<i>b.</i>	<i>Barometer.</i>
1.271 litres per min.	0.00477	750 mm.
1.140	0.00480	—
0.918	0.00478	771
0.850	0.00484	742.5
0.653	0.00490	766
0.637	0.00490	758



<i>Rate of air current.</i>	<i>b.</i>	<i>Barometer.</i>
0.400 litres per min.	0.00470	761 mm.
0.394	0.00483	743
0.200	0.00499	752
0.180	0.00498	758
0.138	0.00475	761

*Mean* 0.00484

Individual results show considerable variation, but *no connection can be traced between the values of b and the rates of air current*, or between the values of *b* and barometric pressure.

In order to make certain of the latter point, a series of experiments was carried out with the ammonia solution under various pressures.

#### *Variation of Pressure.*

In order to aspirate air at less than atmospheric pressure through the ammonia solution, another regulator containing mercury was substituted for the water regulator; it was made of a long, wide glass tube. A stopcock was placed between the flask *A* (Fig. 1) and the meter in order to regulate the air current, and at the same time the pressure in the aspiration flask. Otherwise, the arrangement of the apparatus was exactly as before. The air passing through was measured by the meter at atmospheric pressure. Great care was taken to avoid any leak between the aspiration flask and the meter. The following results were obtained by aspirating in stages.

#### *Pressure in aspiration flask, 623 mm.*

Temperature of solution 19.9°. Rate of air-current, 0.62 litre at the reduced pressure.

<i>Vol. of air aspirated,</i> <i>as read on meter.</i>		<i>NH<sub>3</sub> in solution (g).</i>	<i>log q.</i>	<i>Calculated.</i>
0 litres	3.224 grams		0.5084	(0.5084)
5	2.936		0.4678	0.4675
10	2.676		0.4275	0.4266
15	2.433		0.3861	0.3855
20	2.215		0.3454	0.3447
25	2.013		0.3038	(0.3038)

*Pressure in aspiration flask, 429 mm.*

Temperature of solution, 19.9°. Rate of air-current, 0.40 litre per min.

<i>Vol. of air aspirated.</i>	<i>NH<sub>3</sub> in solution (q).</i>	<i>log q.</i>	<i>log q (cal.).</i>
0 litres	3.419 grams	0.5339	(0.5339)
3	3.131	0.4957	0.4960
6	2.874	0.4585	0.4582
9	2.641	0.4218	0.4203
12	2.417	0.3833	0.3825
15	2.211	0.3446	(0.3446)

The logarithmic law was thus proved to hold for large variations of pressure, and some further results were obtained by the short method.

*Temperature of the solution, 19.9°.*

<i>Pressure in aspiration flask.</i>	<i>b.</i>	<i>Rate of air-current.</i>
941 mm.	0.00642	0.50 litre per min.
623	0.00666	0.62
591	0.00655	0.50
513	0.00666	0.40
435	0.00685	0.50
429	0.00702	0.40

The first result on the table, at a pressure higher than atmospheric, was obtained by forcing air through the solution by means of a water-air pump used as a condenser. The outlet of the pump was connected with a stoneware barrel, and the water was run out by a tube at the bottom. To keep the pressure constant, the excess of air was made to bubble through a tube dipping a certain depth under mercury. The meter was connected to the last flask in the series with a stopcock between them, so that the air was measured by the meter at atmospheric pressure. In calculating the values of *b*, the volumes of air read on the meter (at atmospheric pressure) were reduced to the pressure in the aspiration flask as given by the gauge and the barometer. These results show that a variation of 50 mm. in the pressure produces an inverse variation of about 1 per cent. in the value of *b*. The effect of variation of atmospheric pressure on the value of *b* may therefore be neglected.

*Variation of Temperature.*

It has been already mentioned that the temperature of the solution was noted by means of a thermometer, divided into tenths of a degree,

cemented into the aspiration flask. The thermometer, which was obtained from Messrs. C. E. Müller and Co., was carefully tested; the following readings were obtained.

<i>Thermometer reading.</i>	<i>Real temp.</i>
100·55°	100·15° (boiling water)
34·9	34·8 ( „ ether)
0·13	0·0 (melting ice)

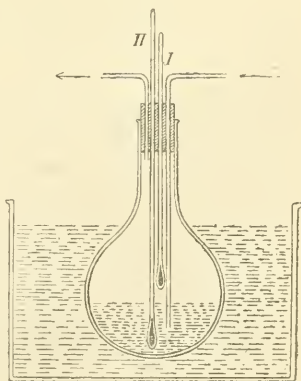
Some time after the experiments in which this thermometer was used had been completed, it was compared with a thermometer which had been directly compared with an air thermometer; the zero point was then 0·3°; allowing for this alteration, the temperatures agreed to 0·1° up to 50°. The real temperatures were therefore taken as 0·1° lower than the thermometer reading, up to 40°; above this temperature, another thermometer was used. The latter thermometer was compared with a simple form of constant-volume air-thermometer, and also with the boiling points of carbon bisulphide and water. The numbers obtained are as follow.

	<i>Real temp.</i>	<i>Thermometer reading.</i>
M. p. of ice	0·0°	0·2°
Air thermometer	11·3	11·5
„	16·6	16·9
„	16·4	16·6
„	36·5	36·6
„	28·6	28·8
B. p. of CS <sub>2</sub> at 750 mm.	45·85	46·1
„ 757 „	46·1	46·4
B. p. of H <sub>2</sub> O 744 „	99·4	99·95

If 0·2° is subtracted from the thermometer reading below 30°, and 0·3° between 30° and 50°, the remaining error is never more than 0·1°. At 60°, 0·4° was subtracted.

An experiment was made in order to determine whether the air and other gases leaving the solution are at the same temperature as the solution itself, the operation being conducted in a flask, Fig. 2, furnished with two thermometers, I and II, one to register the temperature of the solution and the other that of the gas. The results showed that the difference between the temperature of the solution and that of the gases leaving it was not more than 0·2°.

FIG. 2.



Various temperatures up to  $40^{\circ}$  were employed with the apparatus Fig. 1 ; the temperature was kept constant by the addition of hot water when necessary, the pan being surrounded by a flannel jacket for the higher temperatures. The temperature was allowed to fall  $0.2^{\circ}$ , and then hot water was added until it rose  $0.2^{\circ}$  above the stated temperature, then allowed to fall to  $0.2^{\circ}$  below this temperature, and so on. The logarithmic law was found to hold good up to  $46^{\circ}$ , as shown by the following experiments.

Temperature of ammonia solution,  $39.9^{\circ}$ . Rate of air-current, 0.4 litre per min. Pressure in aspiration flask, 737 mm.

<i>Vol. of air aspirated.</i>	<i>NH<sub>3</sub> in solution (g.)</i>	<i>log q.</i>	<i>log q. (cal.).</i>
0 litres	3.273 grams	0.5149	(0.5149)
3	2.889	0.4607	0.4616
3	2.555	0.4074	0.4083
3	2.256	0.3533	0.3550
3	2.004	0.3018	(0.3018)

Temperature of ammonia solution,  $46.1^{\circ}$ . Rate of air-current, 0.4 litres per min. Pressure in aspiration flask, 769 mm.

<i>Vol. of air aspirated.</i>	<i>NH<sub>3</sub> in solution (g.)</i>	<i>log q.</i>	<i>log q. (cal.).</i>
0 litres	1.1651 grams	0.0663	(0.0663)
3	0.8626	1.9358	1.9324
3	0.6394	1.8058	1.7985
3	0.4666	1.6689	1.6646
3	0.3393	1.5306	(1.5306)

This last experiment was carried out with different apparatus from that previously used ; the aspiration flask B. contained only about 25 c.c., and both it and the flask A containing water were jacketted by means of carbon bisulphide vapour, Fig. 3. The carbon bisulphide was boiled in the bulb C, and condensed at D. This arrangement did not give such accurate results as the other, for two reasons, namely (1), only half the amount of ammonia solution was used ; (2), the temperature could not be maintained quite constant ; it rose slowly during the experiment, owing to the decrease in the rate of evaporation of the ammonia ; in the experiment of which the results are given above, the temperature rose  $0.4^{\circ}$  ; the mean temperature is given.

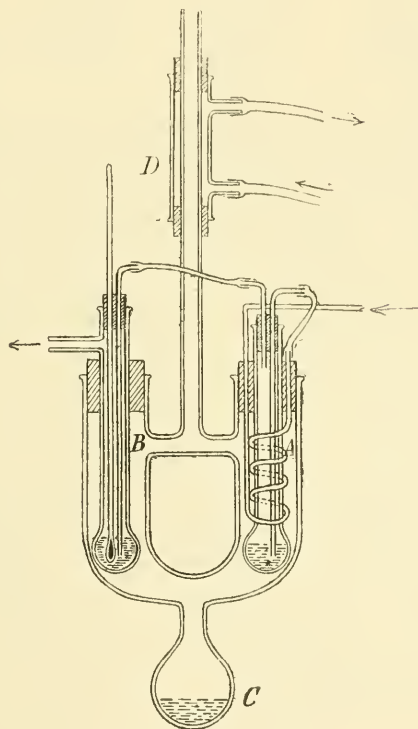
Similar experiments were made at a higher temperature, using chloroform instead of carbon bisulphide, but in that case the logarithmic law did not hold even with considerably more dilute solutions. This is proved by the following results.

Temperature of the solution,  $60.1^{\circ}$ . Rate of air-current, 0.05 litre per min. Pressure in aspiration flask, 758 mm.

<i>Vol. of air aspirated.</i>	<i>NH<sub>3</sub> in solution (q).</i>	<i>log q.</i>	<i>Δ log q.</i>
0 litres	1·645 grams	0·2162	0·0673
0·5	1·409	0·1489	0·0618
1·0	1·222	0·0871	0·0533
1·5	1·081	0·0338	0·0479
2·0	0·968	1·9859	

The values of  $\Delta \log q$  decrease rapidly, instead of remaining constant as at lower temperatures.

FIG. 3.



The following experiment was carried out with a much more dilute solution, but with a similar result.

Temperature of the solution,  $60\cdot2^{\circ}$ . Rate of air-current, 0·1 litre per min. Pressure in aspiration flask, 759 mm.

<i>Vol. of air aspirated.</i>	<i>NH<sub>3</sub> in solution (q).</i>	<i>log q.</i>	<i>Δ log q.</i>
0 litres	0·5998 gram	1·7780	0·0422
0·5	0·5442	1·7358	0·0381
1·0	0·4985	1·6977	0·0361
1·5	0·4588	1·6616	



Using a still more dilute solution,  $\Delta \log q$  became more regular, but there is evidently a large experimental error.

Temperature of the solution,  $59.7^\circ$ . Rate of air-current, 0.1 litre per min. Pressure in aspiration flask, 745 mm.

<i>Vol. of air aspirated.</i>	<i>NH<sub>3</sub> in solution (g).</i>	<i>log q.</i>	<i><math>\Delta \log q</math>.</i>	<i>log q (cal.).</i>
0 litres	0.3370 gram	1.5276		(1.5276)
1	0.2919	1.4652	0.0624	1.4580
2	0.2513	1.4002	0.0650	1.3884
3	0.2127	1.3278	0.0724	1.3188
4	0.1803	1.2560	0.0718	1.2492
5	0.1513	1.1798	0.0762	(1.1798)

A dilute solution of ammonia, at a high temperature, behaves in a similar way to a concentrated solution at a lower temperature; the pressure of the ammonia becomes so great, that the air passing through the solution takes up far more ammonia than would be required by the logarithmic formula. This formula has been proved to hold, for solutions of moderate concentration, between  $0^\circ$  and  $46^\circ$ ; between these limits, therefore, the simplified method of finding the value of  $b$ , described on page 515, may be used; a large number of experiments were carried out in that way at different temperatures.

The following are the results obtained both by the full and the short methods (those at  $13.4^\circ$  have already been given).

*Temperature,  $0^\circ$ .*

<i>Rate of air-current per minute.</i>	<i>b.</i>	<i>Pressure in aspiration flask.</i>
0.825 litre	0.00243	741 mm.
0.605	0.00258	753
0.370	0.00258	747
0.179	0.00270	745

*Mean 0.002615.*

Temperature,  $13.4^\circ$  (see page 516).

*Temperature,  $19.9^\circ$ .*

<i>Rate of air-current per minute.</i>	<i>b.</i>	<i>Pressure in aspiration flask.</i>
0.879 litre	0.00643	760 mm.
0.616	0.00648	759
0.500	0.00650	770
0.421	0.00665	—
0.400	0.00655	766
0.319	0.00645	760
0.220	0.00666	764
0.180	0.00660	748

*Mean 0.00654*

*Temperature, 29.9°.*

<i>Rate of air-current per minute.</i>	<i>b.</i>	<i>Pressure in aspiration flask.</i>
0.860 litre	0.01023	761 mm.
0.433	0.01043	755
0.295	0.01034	758
<i>Mean</i> 0.01033		

*Temperature, 39.9°.*

<i>Rate of air-current per minute.</i>	<i>b.</i>	<i>Pressure in aspiration flask.</i>
0.822 litre	0.01622	754 mm.
0.460	0.01612	766
0.400	0.01670	740
0.292	0.01650	765
<i>Mean</i> 0.01638		

*Temperature, about 46°.*

<i>Temperature.</i>	<i>Rate of air-current per minute.</i>	<i>b.</i>	<i>Pressure.</i>
45.9°	0.10 litre	0.02198	758 mm.
45.5	0.40	0.02227	767
46.0	0.40	0.02026	769
<i>Mean</i> 48.8		<i>Mean</i> 0.02150	

The values of *b* in the last series do not vary regularly with the temperature, and so the mean of the temperatures and the mean of the pressures have been taken, in order to obtain as accurate a result as possible. The mass of water present in the ammonia solution in the aspiration flask in these experiments was only half that in the experiments at lower temperatures. It has been shown that, if the mass of water remains constant, the rate of escape of the ammonia is proportional, within certain limits, to the amount of ammonia present. It may be inferred from this that, if the amount of water is altered, within certain limits, the rate of escape of the ammonia will be inversely proportional to the amount of water present, supposing the quantity of ammonia to remain constant. The following are the results of experiments made to prove this point.

<i>t°.</i>	<i>Vol. of solution taken (15°).</i>	<i>b.</i>	<i>b corrected to 50 c.c.</i>	<i>b found when 50 c.c. were used.</i>
19.9°	25 c.c.	0.01321	0.00660	0.00654
13.4	20	0.01245	0.00498	0.00485
13.4	20	0.01251	0.00500	0.00485

The agreement is very good with the 25 c.c. experiment, but not so good with the smaller volume when the experimental error was greater

The value of  $b$  obtained with the small flask in carbon bisulphide vapour was corrected in the same way, that is, it was halved.

At each temperature various rates of air-current were employed, but no certain connection has been traced between the rate of air-current and the value of  $b$ , although there appears to be a tendency for the latter to increase as the former decreases.

Attempts were made to discover some simple connection between the rate of escape of the ammonia, measured by  $b$ , and the temperature of the solution. After several trials, it was found that the relation is accurately represented by the equation  $\log b = a + \beta t$ , where  $a$  is a constant (namely,  $\log b$  at  $0^\circ$ ),  $\beta$  a constant, and  $t$  the number of degrees in the temperature on the centigrade scale. The value of  $\beta$ , calculated between  $0^\circ$  and  $39.9^\circ$ , is 0.01997; the experiments at  $46^\circ$  are not so accurate, and are therefore not employed for this purpose. The results are given in the following table.

$t^\circ$ .	$b$ .	$\log b$ .	$\log b$ (cal.).
$0^\circ$	0.002615	$\bar{3}.4172$	( $\bar{3}.4175$ )
13.4	0.00485	$\bar{3}.6857$	$\bar{3}.6851$
19.9	0.00654	$\bar{3}.8156$	$\bar{3}.8149$
29.9	0.01033	$\bar{2}.0141$	$\bar{2}.0146$
39.9	0.01638	$\bar{2}.2143$	( $\bar{2}.2143$ )
45.8	0.02150	$\bar{2}.3324$	$\bar{2}.3321$

It will be seen that the agreement between the observed and calculated values is extremely close. There is no reason (except that of convenience) for reckoning the temperatures from zero; if absolute temperatures are taken, an exactly similar expression can be found.

It should be mentioned that no correction has been applied for the expansion of the ammonia solution on heating. The amount of expansion was, however, proved to be very small. The density of the solution made use of was found at different temperatures by weighing in a specific gravity bottle.

Temp.	Weight of 50 c.c.	Vol. of 1 gram.
$0^\circ$	48.801 grams	1.025 c.c.
20.2	48.594	1.029
30.1	48.437	1.032
39.6	48.264	1.036

The total amount of expansion between  $0^\circ$  and  $40^\circ$  is thus only about 1 per cent., very little more than that of pure water. The mass of the water was the same in the experiments at different temperatures, and it is difficult to say what would be the nature of a correction for alteration in volume only. It appears, however, to be unnecessary.

It will be interesting to combine the two equations,  $\log q = a - bV$ , and  $\log b = a + \beta t$ . Let  $a = \log a'$ , and  $a = \log a'$ ,

thus  $q = a' (10)^{-bV}$ , and  $b = a' (10)^{\beta t}$ .

Therefore  $q = a' \cdot 10^{-a'V \cdot 10^{\beta t}}$ , or  $\log q = a - y$ , if  $\log y = a + \log V + \beta t$ .

If a certain volume of air is aspirated through an aqueous ammonia solution at a constant temperature (between  $0^\circ$  and  $46^\circ$ ), the amount of ammonia left in solution can be at once calculated from the above expression.

$q$  = amount of ammonia left in solution.

$a$  = log of amount of ammonia in the solution at the beginning of the aspiration.

$a$  = log of value of  $b$  at  $0^\circ$ .

$V$  = volume of air aspirated through the solution, reckoned as *dry* air at the temperature and pressure (by gauge) of the solution. Before passing into the solution, the air is saturated with moisture at the temperature of the solution.

$\beta$  = a constant.

$t$  = temperature of the solution in degrees centigrade.

In working out this expression, the mass of water has been assumed to be constant. If it varies, the equation  $\log q = a - bV$  will become  $\log q = a - Vb/m$  where  $m$  = mass of water present. It will only hold, however, within certain limits.

The final equation then becomes  $\log q = a - y$ , where  $\log y = a - \log m + \beta t + \log V$ .

If the ammonia solution were simply a mechanical mixture of water and ammonia molecules, the ammonia would be carried off according to the logarithmic equation,  $\log q = a - bV$ , just as if, for example, 10 c.c. of water were added to and mixed with a litre of ammonia solution, and then 10 c.c. of the solution were withdrawn, 10 c.c. more of water were added, another 10 c.c. of the solution withdrawn, and so on; then the amount  $q$  of ammonia present would be represented by the same expression,  $\log q = a - bV$ ,  $V$  being the volume of water that had been added to (or withdrawn from) the solution. The ammonia is actually carried off by a current of air in this way from dilute solutions, but the rate of escape from a concentrated solution is far greater than required by this equation, probably owing to the less attraction (in proportion to the amount of ammonia present) between the water and the ammonia in concentrated solutions. The author is at present engaged in further experiments, the object of which is to discover the effect of the addition of various substances to the solution on the rate of escape of the ammonia. He is also investigating the vapour-pressure of ammonia solution by a statical method. In conclusion, he

wishes to express his thanks to Mr. G. A. S. Atkinson, of Cardiff, for his able assistance in the latter part of the work.

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*Appendix.*

*Temperature of solution, 0°.*

<i>Vol. of air in litres read on meter.</i>	<i>Rate of air- current in litres.</i>	<i>Temp. of air.</i>	<i>Press. in aspiration flask.</i>		<i>*q<sub>1</sub> in grams.</i>	<i>*q<sub>2</sub> in grams.</i>	<i>b.</i>
27	0·825	13°	752 mm.	752	3·643	3·153	0·00247
19	0·605	15	766	766	3·436	3·087	0·00262
20	0·370	15	—	—	3·666	3·275	0·00262
13·5	0·179	15	758	758	3·731	3·445	0·00275

*Temperature of solution, 13·4°.*

25	1·271	14	750	750	3·566	2·724	0·00477
40	1·140	12	—	—	3·686	2·377	0·00480
34	0·918	11	771	771	3·707	2·549	0·00478
17	0·850	12	742·5	742·5	3·597	2·981	0·00484
19	0·653	16	766	766	3·537	2·870	0·00490
30	0·637	15	758	758	3·678	2·641	0·00490
21	0·400	15	761	761	3·492	2·788	0·00470
20·5	0·394	14	743	743	3·620	2·894	0·00483
30	0·200	14	752	760·5	3·649	2·591	0·00499
19	0·180	16	751	758	3·509	2·833	0·00498
12·8	0·138	15	761	761	3·648	3·175	0·00475

*Temperature of solution, 19·9°.*

25	0·879	17	760	760	3·558	2·465	0·00643
20	0·616	16	759	759	3·465	2·576	0·00648
24	0·500	14	770	770	3·620	2·523	0·00650
17	0·421	17	—	—	3·614	2·792	0·00665
20	0·400	17	766	766	3·328	2·467	0·00655
20	0·319	21	760	760	3·319	2·484	0·00645
18	0·220	17	764	764	3·738	2·844	0·00666
18	0·180	17·5	748	755	3·323	2·529	0·00660

\*  $q_1$  and  $q_2$  are the quantities of ammonia in the aspiration flask at the beginning and end, respectively, of each experiment.



*Temperature of solution, 29.9°.*

<i>Vol. of air in litres read on meter.</i>	<i>Rate of air- current in litre.</i>	<i>Temp. of air.</i>	<i>Press. in aspiration flask.</i>	<i>Bar.</i>	<i>q<sub>1</sub> in grams.</i>	<i>q<sub>2</sub> in grams.</i>	<i>b.</i>
22	0.860	18°	761 mm.	761	3.241	1.910	0.01023
17.8	0.433	19	755	755	3.450	2.235	0.01043
21	0.295	18	758	758	3.661	2.198	0.01034

*Temperature of solution, 39.9°.*

12	0.822	16	754	754	2.562	1.591	0.01622
13	0.460	17	766	766	2.996	1.797	0.01612
12	0.400	19	740	740	3.273	2.004	0.01670
14	0.292	16	765	765	3.208	1.823	0.01650

*Small aspiration flask. Temperature of solution, 45.9°.*

4	0.10	16°	758 mm.	766	1.682	1.079	$\frac{b}{2}$ 0.02198
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*Temperature of solution, 45.5°.*

4	0.40	13	767	772	1.613	1.025	0.02227
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*Temperature of solution, 46.0°.*

12	0.40	14	769	774	1.165	0.339	0.02026
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*Temperature of solution, 19.9°.*

12	0.40	16	744	744	1.719	1.192	0.00660
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*Temperature of solution, 13.4°.*

18	0.360	15	—	—	1.729	1.043	$\frac{2}{5b}$ 0.00498
18	0.314	18	758	758	1.760	1.067	0.00500

*Variation of pressure. Temperature of solution, 19.9°.*

26	0.50	18	941	769	3.349	2.457	$\frac{b}{b}$ 0.00642
25	0.62	14.5	623	762	3.224	2.013	0.00666
18	0.50	16	591	763	3.339	2.356	0.00655
14	0.40	15	513	753	3.314	2.426	0.00666
11	0.50	13	435	760	3.336	2.457	0.00685
15	0.40	15	429	772	3.419	2.211	0.00702

## LV.—*Note on The Liquefaction of Hydrogen and Helium.*

By Prof. JAMES DEWAR.

IN a paper entitled "The Liquefaction of Air and Research at Low Temperatures," read before the Chemical Society and published in the Proceedings, No. 158, an account is given of the history of the liquid hydrogen problem and the result of my own experiments up to the end of the year 1895. The facts are substantially as follows.

Wroblewski made the first conclusive experiments on the liquefaction of hydrogen in January, 1884. He found that the gas cooled in a capillary glass tube to the boiling point of oxygen, and expanded quickly from 100 to 1 atmos., showed the same appearance of sudden ebullition, lasting for a fraction of a second, as Cailletet had seen in his early oxygen experiments. No sooner had the announcement been made, than Olszewski confirmed the result by expanding hydrogen from 190 atmos., previously cooled to the temperature given by liquid oxygen and nitrogen evaporating under diminished pressure. Olszewski, however, declared in 1884 that he saw colourless drops, and by partial expansion to 40 atmos. the liquid hydrogen was seen by him running down the tube. Wroblewski could not confirm Olszewski's results, his hydrogen being always obtained in the form of what he called a "liquide dynamique," or the appearance of an instantaneous froth. The following extract from Wroblewski's paper (*Compt. rend.*, 1885, 100, 981) states very clearly the results of his work on hydrogen:—  
 "L'hydrogène soumis à la pression de 180 atm. jusqu'à 190 atm. refroidi par l'azote bouillant dans la vide (à la température de sa solidification) et détendu brusquement sous la pression atmosphérique présente une mousse bien visible. De la couleur grise de cette mousse, où l'œil ne peut distinguer des gouttelettes incolores, on ne peut pas encore deviner quelle apparence aurait l'hydrogène à l'état de liquide statique et l'on est encore moins autorisé à préciser s'il a ou non une apparence métallique.

"J'ai pu placer dans cette mousse ma pile thermo-électrique et j'ai obtenu suivant les pressions employées des températures de  $-208^{\circ}$  jusqu'à  $-211^{\circ}$  C. Je ne peux pas encore dire dans quelle relation se trouvent ces nombres avec la température réelle de la mousse et la température d'ébullition de l'hydrogène sous la pression atmosphérique, puisque je n'ai pas encore la certitude que la faible durée de ce phénomène ait permis à la pile de se refroidir complètement. Néanmoins, je crois aujourd'hui de mon devoir de publier ces résultats, afin de préciser l'état actuel de la question

de la liquéfaction de l'hydrogène." It is well to note that the lowest thermo-electric temperature recorded by Wroblewski during the adiabatic expansion of the hydrogen, namely,  $-211^{\circ}$  is really equivalent to a much lower temperature on the gas thermometer scale. The most probable value is  $-230^{\circ}$ , and this must be regarded as the highest temperature of the liquid state, or the critical point of hydrogen according to his observations. The above methods having failed to produce "static" hydrogen, Wroblewski suggested that the result might be attained by the use of hydrogen gas as a cooling agent. From this time until his death in the year 1888, Wroblewski devoted his time to a laborious research on the isothermals of hydrogen at low temperatures. The data thus arrived at enabled him, by the use of Van der Waal's formulæ, to calculate the critical constants and boiling point of liquid hydrogen.

Olszewski returned to the subject in 1891, repeating and correcting his old experiments of 1884, which Wroblewski had failed to confirm, in a glass tube 7 mm. in diameter instead of one of 2 mm., as in the early trials. He says, "On repeating my former experiments, I had no hope of obtaining a lower temperature by means of any cooling agent, but I hoped that the expansion of hydrogen would be more efficacious, on account of the larger scale on which the experiment was made." The result of these experiments Olszewski describes as follows, "The phenomenon of hydrogen ebullition, which was then observed, was much more marked and much longer than during my former investigations in the same direction. *But even then I could not perceive any meniscus of liquid hydrogen.*" Further, "The reason for which it has not been hitherto possible to liquefy hydrogen in a static state, is that there exists no gas having a density between those of hydrogen and of nitrogen, and which might be for instance 7—10 (H 1). Such a gas could be liquefied by means of liquid oxygen or air as cooling agent, and be afterwards used as a frigorific menstruum in the liquefaction of hydrogen."

Professor Olszewski, in 1895, determined the temperature reached in the momentary adiabatic expansion of hydrogen at low temperatures; just as Wroblewski had done in 1885, only he employed a platinum resistance thermometer instead of a thermo-junction.

For this purpose, he used a small steel bottle of 20 or 30 c.c. capacity, containing a platinum resistance thermometer; in this way, temperatures were registered which were regarded as those of the critical and boiling points of liquid hydrogen, a substance which *could not be seen* under the circumstances, and was only assumed at the most to exist for a second or two during the expansion of the gaseous hydrogen in the small steel bottle.

The results arrived at by Wroblewski and Olszewski are given in the following table.

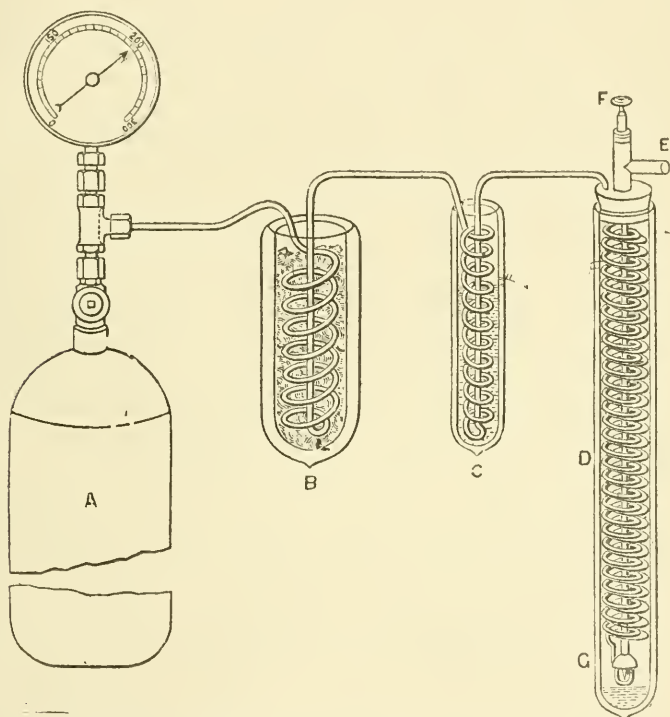
	Wroblewski, 1885.	Olszewski, 1895.
Critical temperature...	- 240°	- 234°
Boiling point.....	- 250°	- 243°
Critical pressure .....	13At.	20At.

The moment the critical point is approximately defined, the boiling point is roughly known, and the critical pressure can be inferred from analogy with the behaviour of other substances.

In a paper published in the *Phil. Mag.*, September, 1884, "On the Liquefaction of Oxygen and the Critical Volumes of Fluids," the suggestion was made that the critical pressure of hydrogen was wrong, and that instead of being 99 atmos. (as deduced by Sarrau from Amagat's isothermals), the gas had probably an abnormally low value for this constant. This view was substantially confirmed by Wroblewski finding a critical pressure of 13·3 atoms., or about one-fourth of that of oxygen. The *Chemical News* (September 7, 1894) contains an account of the stage the author's hydrogen experiments had reached at that date. The object was to collect liquid hydrogen at its boiling point, in an open vacuum vessel, which is a much more difficult problem than seeing the liquid in a glass tube under pressure and at a higher temperature. In order to raise the critical point of hydrogen to about - 200°, from 2 to 5 per cent. of nitrogen or air was mixed with it. This is simply making an artificial gas containing a large proportion of hydrogen which is capable of liquefaction by the use of liquid air. The results are summed up in the following extract from the paper. "One thing can, however, be proved by the use of the gaseous mixture of hydrogen and nitrogen, namely, that by subjecting it to a high compression at a temperature of - 200° and expanding the resulting liquid into air, a much lower temperature than anything that has been recorded up to the present time can be reached. This is proved by the fact that such a mixed gas gives, under the conditions, a paste or jelly of solid nitrogen, evidently giving off hydrogen, because the gas coming off burns fiercely. Even when hydrogen containing only some 2 to 5 per cent. of air is similarly treated, the result is a white, solid matter (solid air) along with a clear liquid of low density, which is so exceedingly volatile that no known device for collecting has been successful."

The report of a Friday Evening Lecture on "New Researches on Liquid Air" (*Proc. Roy. Inst.*, 1896) contains a drawing of the apparatus employed for the production of a jet of hydrogen containing visible liquid. This is reproduced in the figure. A represents one of the hydrogen cylinders; B and C, vacuum vessels containing carbonic acid under exhaustion and liquid air respectively; D is the coil, G the

pin-hole nozzle, and F the valve. By means of this jet, liquid air can be quickly transformed into a hard solid. It was shown that such a jet could be used to cool bodies below the temperature that it is possible to reach by the use of liquid air, but all attempts to collect the liquid hydrogen from the jet in vacuum vessels failed. No other investigator has, so far, improved on the results the author described in the Proceedings of the Chemical Society (No. 158), 1895, or, indeed, touched the subject since that date. The type of



APPARATUS USED IN THE PRODUCTION OF THE LIQUID HYDROGEN JET.

apparatus used in these experiments worked well, so it was resolved to construct a much larger liquid air plant, and to combine with it circuits and arrangements for the liquefaction of hydrogen, which will be described in a subsequent paper. This apparatus took a year to build up, and many months have been occupied in testing and making preliminary trials. The many failures and defeats need not be detailed.

On May 10th of this year, starting with hydrogen cooled to  $-205^{\circ}$ , and under a pressure of 180 atmospheres, escaping continuously from



the nozzle of a coil of pipe at the rate of about 10 to 15 cub. ft. per minute, in a vacuum vessel doubly silvered and of special construction, all surrounded with a space kept below  $-200^{\circ}$ , liquid hydrogen commenced to drop from this vacuum vessel into another doubly isolated by being surrounded with a third vacuum vessel. In about 5 minutes, 20 cubic centimetres of liquid hydrogen were collected, when the hydrogen jet froze up, from the accumulation of air in the pipes frozen out from the impure hydrogen. The yield of liquid was about 1 per cent. of the gas. The hydrogen in the liquid condition is clear and colourless, showing no absorption spectrum, and the meniscus is as well defined as in the case of liquid air. The liquid must have a relatively high refractive index and dispersion, and the density appears also to be in excess of the theoretical density, namely, 0.18 to 0.12, which we deduce respectively from the atomic volume of organic compounds, and the limiting density found by Amagat for hydrogen gas under infinite compression. Yet this may be a delusion due to its high dispersion. A preliminary attempt to weigh a small glass bulb in the liquid made the density about 0.08. My old experiments on the density of hydrogen in palladium gave a value for the combined element of 0.62, and it will be interesting to find the accurate density of the liquid substance at its boiling point. Not having arrangements at hand to determine the boiling point, other than a thermo-junction which gave entirely fallacious results, experiments were made to prove the excessively low temperature of the boiling fluid. In the first place, if a long piece of glass tubing, sealed at one end and open to the air at the other, is cooled by immersing the closed end in the liquid hydrogen, the tube immediately fills, where it is cooled, with solid air; a small tube containing liquid oxygen became a bluish solid. A first trial of putting the liquid hydrogen under exhaustion gave no appearance of transition into the solid state. The liquid hydrogen in its vacuum tube, which is immersed in liquid air so that the external wall of the vacuum vessel is maintained at about  $-190^{\circ}$ , is found to evaporate at a rate not far removed from that of liquid air from a similar vacuum vessel under the ordinary conditions of storage. This leads me to the conclusion that, with proper isolation, it will be possible to manipulate with liquid hydrogen as easily as with liquid air. The second experiment was made with a tube containing helium.

The Cracow Academy *Bulletin* for 1896 contains a paper by Professor Olszewski, entitled, "A Research on the Liquefaction of Helium," in which he states, "As far as my experiments go, helium remains a permanent gas and apparently is much more difficult to liquefy than hydrogen." In a paper of my own in the Proceedings of the Chemical

Society, No. 183 (1896—7), in which the separation of helium from Bath gas was effected by a liquefaction method, the suggestion was made that the volatility of hydrogen and helium would probably be found close together, just like those of fluorine and oxygen. Having a specimen of purified helium, which had been extracted from Bath gas, sealed up in a bulb with a narrow tube attached, the latter was placed in liquid hydrogen, when a distinct liquid was seen to condense. The same experiment repeated, only using liquid air evaporating in a vacuum gave no trace of condensation. From this result, it would appear that there cannot be any great difference between the boiling points of helium and hydrogen.

All known gases have now been condensed into liquids which can be manipulated at their boiling points under atmospheric pressure in suitably arranged vacuum vessels. With hydrogen as a cooling agent, we shall get within 20 or 30 of the zero of absolute temperature and its use will open up an entirely new field of scientific inquiry. Even as great a man as James Clerk Maxwell had doubts as to the possibility of ever liquefying hydrogen, see *Scientific Papers*, 2, 412. In concluding his lectures on the non-metallic elements, delivered at the Royal Institution in 1852 and published the following year, Faraday said (See Faraday's "Lectures on the Non-metallic Elements" p. 292—3), "There is reason to believe we should derive much information as to the intimate nature of these non-metallic elements, if we could succeed in obtaining hydrogen and nitrogen in the liquid or solid form. Many gases have been liquefied; the carbonic acid gas has been solidified, but hydrogen and nitrogen have resisted all our efforts of the kind. Hydrogen in many of its relations acts as though it were a metal; could it be obtained in a liquid or solid condition, the doubt might be settled. This great problem, however, has yet to be solved; nor should we look with hopelessness on this solution when we reflect with wonder—and as I do almost with fear and trembling—on the powers of investigating the hidden qualities of these elements—of questioning them, making them disclose their secrets and tell their tales—given by the Almighty to man."

Faraday's expressed faith in the potentialities of experimental inquiry in 1852 has been justified forty-six years afterwards by the production of liquid hydrogen in the very laboratory in which all his epoch-making researches were executed. The "doubt" has now been settled, hydrogen does not possess in the liquid state the characteristics of a metal. No one can predict the properties of matter near the zero of temperature. Faraday liquefied chlorine in the year 1823. Sixty years afterwards, Wroblewski and Olszewski produced liquid air, and now, after a fifteen years' interval, the remaining gases, hydrogen and helium, appear as static liquids. Considering the step from the

liquefaction of air to that of hydrogen is relatively as great in the thermodynamic sense as that from liquid chlorine to liquid air, the fact that the former result has been achieved in one-fourth the time needed to accomplish the latter proves the greatly accelerated race of scientific progress in our time.

The efficient cultivation of this field of research depends upon combination and assistance of an exceptional kind, but in the first instance money must be available, and the members of the Royal Institution deserve my especial gratitude for their handsome donations to the conduct of this research. Unfortunately, its prosecution will demand a further large expenditure. It is my duty also to acknowledge that at an early stage of the enquiry the Hon. Company of Goldsmiths helped low temperatures investigation by a generous donation to the Research Fund.

During the whole course of the low temperature work, carried out at the Royal Institution, the invaluable aid of Mr. Robert Lennox has been at my disposal, and it is not too much to say that, but for his engineering skill, manipulative ability, and loyal perseverance, the present successful issue might have been indefinitely delayed. My thanks are also due to Mr. J. W. Heath for valuable assistance in the conduct of these experiments.

#### *Addendum.*

Since the above paper was written, both the boiling point and specific gravity of hydrogen have been determined. The boiling point in the meantime given by the use of a platinum resistance thermometer involves, however, extrapolation of the curve correlating temperature and resistance; the result is that the boiling point of hydrogen is  $-238^{\circ}$  C. or  $35^{\circ}$  absolute. At this temperature, the tension of liquid air (which, of course, becomes solid) is less than 0.002 mm. The resistance of the thermometer used was 5.338 ohm at the melting point of ice, and this was reduced to 0.129 ohms when placed in boiling hydrogen. The absolute zero in platinum degrees of this thermometer was  $-263.27$ , and the temperature measured on this scale is  $-256.29^{\circ}$  or  $6.38^{\circ}$  from the point where the conductivity of the platinum would become infinite. The resistance of the platinum in the liquid hydrogen is reduced to nearly  $\frac{1}{11}$ th of what it is in liquid oxygen. It will be necessary to find out the electric conductivity of the fluid itself, and to repeat the observations with other thermometers, before we can arrive at more definite conclusions. The vapour of hydrogen at its boiling point is about eight times denser than the gas at ordinary temperatures, or it has about half the density of air, whilst the vapour coming off from liquid

air at its boiling point is somewhat less than four times the density of air at the ordinary temperature. By evaporation in a vacuum, the temperature of liquid hydrogen will be lowered from  $10^{\circ}$  to  $15^{\circ}$ , but it will be practically impossible (so far as we can anticipate the results of experiment) to reach a lower temperature than  $-250^{\circ}$  C or  $20^{\circ}$  absolute by this means. At present, we can see no way of bridging over the last 20 to 25 degrees, and therefore the approach to the zero of absolute temperature and the study of matter and energy under such conditions must be confined to temperatures above  $25^{\circ}$  absolute.

The density of liquid hydrogen has been approximately determined by evaporating some 10 c.c. of the liquid, and collecting and measuring the gas produced, thereby ascertaining its weight. In this way, 8.15 litres at  $14^{\circ}$  C. and 753 mm. were collected over water from between 9 and 10 c.c. of liquid hydrogen. It appears, therefore, that the density of the liquid is about 0.07, using whole numbers as the calculation works out to 0.068 nearly. Liquid hydrogen is, therefore, a very deceptive fluid so far as appearance goes. The fact of its collecting so easily, dropping so well, and having such a well defined meniscus induced me to believe that the density might be about half that of liquid air. It was a great surprise to find the density only  $\frac{1}{14}$ th of water. Liquid marsh gas was the lightest known liquid, the density at its boiling point being 0.417, but liquid hydrogen has only  $\frac{1}{6}$ th the density of this substance. The density of occluded hydrogen in palladium being 0.62, it is eight times denser than the liquid.

Hydrogen in the liquid state is 100 times denser than the vapour it is giving off at its boiling point, whereas liquid oxygen is 255 times denser than its vapour. It appears, therefore, that the atomic volume of liquid hydrogen at its boiling point is 14.3, as compared with 13.7 for oxygen under similar circumstances. In other words, they are nearly identical. From this we can infer that the critical pressure need not exceed 15 atmospheres. The extraordinary properties theory requires hydrogen should possess, especially as regards specific and latent heat, become more intelligible from the moment we know that the density is so small. In other words, when we compare the properties of equal volumes of liquid hydrogen and air under similar corresponding temperatures, they do not differ more than might be anticipated.

ROYAL INSTITUTION.



# LVI.—*Action of Formaldehyde on Amines of the Naphthalene Series. Part I.*

By GILBERT THOMAS MORGAN, B.Sc.

THE interaction of formaldehyde and the amines of the benzene series has been extensively studied in the past, especially since some of the compounds formed have been employed in the synthetical production of colouring matters. The production of the acridine yellows from condensation products of formaldehyde with certain of the benzenoid metadiamines and the synthesis of pararosaniline and its homologues (Meister, Lucius and Brüning, D.R.P., 53937) may be quoted in illustration.

When formaldehyde acts on the primary benzenoid amines, the initial stage of the reaction gives rise to a series of unstable compounds which can be converted, usually by the action of acids, into more stable derivatives. Tollens found (*Ber.*, 1884, 17, 657, and *ibid.*, 1885, 18, 3300) that when formaldehyde was added to aniline suspended in water, anhydroformaldehyde-aniline,  $C_6H_5N:CH_2$ , was produced, and Eberhardt and Welter (*Ber.*, 1894, 27, 1804), by the action of these substances in alcoholic potash, obtained methylenediphenyldi-imide,  $CH_2(NH \cdot C_6H_5)_2$ . These two compounds are very unstable; on boiling with solvents, they pass into oily, uncrystallisable forms, and on hydrolysis with dilute acids, aniline and formaldehyde are regenerated. When either of these compounds is heated with aniline and aniline hydrochloride, a rearrangement occurs whereby the methylene group becomes attached to two aromatic nuclei, and diamidodiphenylmethane is produced (Meister, Lucius, and Brüning, *loc. cit.*, and Eberhardt and Welter, *loc. cit.*). This attachment may take place in two stages, for Meister, Lucius, and Brüning (D.R.P., 87934) found that the intermediate compound, paramidobenzylaniline, is capable of existence, and on warming with dilute acids passes into the diphenylmethane derivative.

Orthotoluidine and formaldehyde give rise to a precisely similar series of compounds (Eberhardt and Welter, *loc. cit.*, and Meister, Lucius, and Brüning, D.R.P., 55565, 1890).

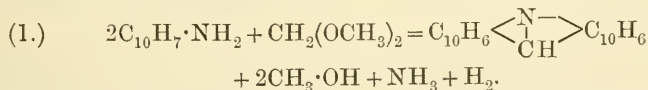
Paratoluidine yields an anhydro-base,  $C_7H_7N:CH_2$  (Tollens, *Ber.*, 1895, 18, 3302), and also methylenediparatolyldi-imide (Eberhardt and Welter, *loc. cit.*); the latter, when warmed with paratoluidine and its hydrochloride, yields a small quantity of diamidodiparatolylmethane in which the methylene group probably occupies the ortho-position in each of the aromatic nuclei. Tröger, by the action of methylal on paratoluidine hydrochloride, obtained a base,  $C_{17}H_{18}N_2$ , to which he ascribed the



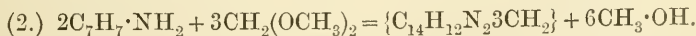
constitution  $C_7H_7 \cdot N : CH \cdot CH_2 \cdot CH : N \cdot C_7H_7$  (*J. pr. Chem.*, 1887, 36, 226). In the case of dimethylaniline, a preliminary attachment of methylene to the side chain is impossible, and accordingly tetramethyldiamidodiphenylmethane is the first product of the action of formaldehyde on the tertiary base (Tröger, *loc. cit.*). These examples indicate that, in the benzene series, formaldehyde is one of those numerous reagents which first attack the side chain, when, by rearrangement under the influence of acids, the methylene group enters the nucleus.

The action of formaldehyde on the two naphthylamines and their derivatives has been far less extensively studied. Reed (*J. pr. Chem.*, 1886, 35, 314) examined the products of reaction between methylal, acetone, and  $\beta$ -naphthylamine and obtained naphthacridine and a base,  $C_{24}H_{20}N_2$ , melting at  $202-203^\circ$ , besides a small amount of methyl- $\beta$ -naphthoquinoline. By acting with methylal alone on  $\beta$ -naphthylamine, he obtained nothing but naphthacridine. O. Fischer prepared a series of naphthimidazoles from formaldehyde and substituted 1:2-naphthylene diamines (*Ber.*, 1894, 27, 2773), and in this case the methylene group remained attached to the side chains. Formaldehyde and 1:2-aminonaphthalenesulphonic acid produce diamidodinaphthylmethanedisulphonic acid, in which the methylene group has entered the ring in a para-position relatively to the amido-groups (Meister, Lucius, and Brüning (D.R.P., 84379, 1894).

In the following experiments,  $\beta$ -naphthylamine was treated with formaldehyde under various conditions, in order to see how far the course of the reaction is comparable with that obtaining in the benzene series. It will be seen that condensation between the aldehyde and the base may be accompanied by the elimination of ammonia and hydrogen. The tendency to form compounds in which the elimination of water is accompanied by the removal of hydrogen has already been noted in the formation of alkyl naphthocinchonic acids by the action of aldehydes (other than formaldehyde) and pyruvic acid on  $\beta$ -naphthylamine (Doebner, *Ber.*, 1894, 27, 2020). Reed (*loc. cit.*) found that methylal acting on  $\beta$ -naphthylamine hydrochloride in excess of acid produced naphthacridine melting at  $216^\circ$ .



Tröger (*loc. cit.*), performing a similar experiment on paratoluidine obtained a compound which indicated that a simple condensation had occurred between three molecules of the aldehyde and two of the base.



In my experiments, naphthylamine not only reacts according to

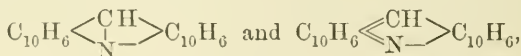
Reed's equation, but also in a manner analogous to that of paratoluidine.

A third mode of reaction occurs, giving rise to a small quantity of product in which hydrogen alone is eliminated, probably owing to the oxidising action of some of the other substances present.

Besides Reed's naphthacridine (m. p. 216°), another substance of like composition,  $C_{21}H_{13}N$ , is produced according to the first equation; this crystallises in orange-coloured needles, melts at 225—226°, and behaves in a peculiar manner with hydrogen chloride. When triturated with concentrated hydrochloric acid, or submitted to the action of the dry gas, a green hydrochloride is produced, from which the original base may be regenerated by the action of aqueous alkalis; but on passing hydrogen chloride into a solution of the base in glacial acetic acid, or in benzene, a yellow hydrochloride is precipitated which yields Reed's naphthacridine on treatment with alkalis. The same change is brought about by boiling the glacial acetic acid solution of the orange-coloured base for several hours; and also by the action of certain solvents, as, for example, acetone. When the substance is boiled for some days with acetone, orange needles no longer separate on cooling, but amber-coloured prisms of naphthacridine are produced; the conversion, however, when induced by this means is slow and incomplete. On the other hand, it appears that naphthacridine itself can be partially reconverted into the orange-coloured base by long boiling with a solution of sodium amyl oxide in amylic alcohol, but hitherto only about 30 per cent. of the naphthacridine has been changed into its isomeride.

The relationship between the constitution of these two bases must be a simple one, and it is quite conceivable that the orange base may be a quinonoid form of naphthacridine.

The formulæ for the two bases would be



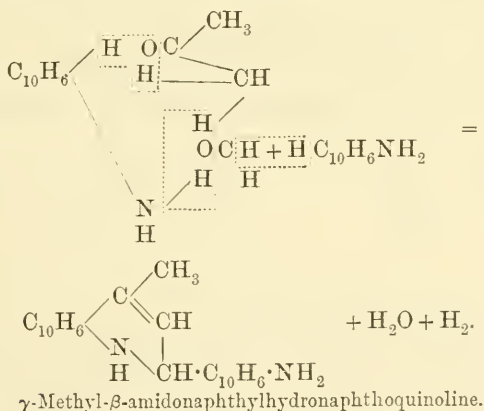
the former corresponding with naphthacridine and the latter with the orange-coloured base. The latter will be referred to as *isonaphthacridine*.

The formation of green salts from the orange-coloured isonaphthacridine is a remarkable example of colour change. In the benzene series, a colour change in the opposite sense is observed in the production of a yellow salt from green nitrosodimethylaniline. A remarkably similar case presents itself in the naphthalene series, which, even if only a coincidence, is worthy of note.  $\alpha$ -Nitroso- $\beta$ -naphthol is a *yellow* compound of admittedly quinonoid structure, and is usually represented by the formula  $O:C_{10}H_6:NOH$ . This substance is acidic,

and its alkali salts are *green* (Ilinsky, *Ber.*, 1884, 17, 2585). The imido-compound which is obtained from nitroso- $\beta$ -naphthol is also green, and has the constitution  $\text{NH}\cdot\text{C}_{10}\text{H}_6\cdot\text{NOH}$  (*Ber.*, 1886, 19, 343). It is quite possible that this colour change is characteristic of certain derivatives of  $\beta$ -naphthaquinone.

It will be somewhat difficult to obtain direct evidence in support of the two formulæ suggested for the naphthacridines, for in the case of isonaphthacridine it is<sup>1</sup> difficult to select reagents which will act on it without first converting it into the more stable naphthacridine. When isonaphthacridine is heated with methylic or ethylic iodide in sealed tubes at 150°, a yellow methiodide or ethiodide is produced; both these substances, on treatment with alcoholic ammonia, give rise to naphthacridine, and are identical with the iodide produced by the alkyl iodides and this base. The salts of naphthacridine are all yellow, and the hydrochloride, hydriodide, methiodide and ethiodide possess the noteworthy property of crystallising from aniline without decomposition.

Reed supposed that acetone was necessary for the production of the base melting at 203°, to which he gave the formula  $C_{24}H_{20}N_2$ , assuming it to be formed in the following manner.



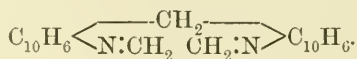
It has been shown conclusively, by the experiments described below, that acetone takes no part in the formation of this base, and that it is produced simply from formaldehyde and  $\beta$ -naphthylamine according to the following equation.



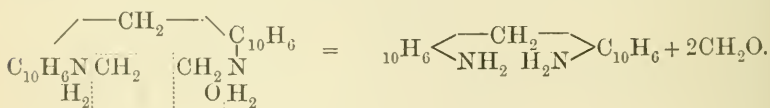
This compound is one of the products of the action of methylal on  $\beta$ -naphthylamine hydrochloride, and is also obtained when formaldehyde acts on the base in alcoholic, glacial acetic, or ethereal solutions. The percentage of carbon required by the two formulæ,

$C_{24}H_{20}N_2$  and  $C_{23}H_{18}N_2$ , is the same, namely, 85.71, but the second contains less hydrogen and more nitrogen than the former, and the analyses given below agree more closely with the latter formula.

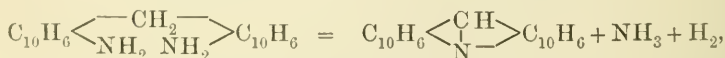
Many experiments were instituted with a view of determining more exactly the constitution of the base. From the above equation expressing its formation, it will be seen that the compound contains three methylene groups associated with two naphthylamine residues,  $C_{10}H_6N(\beta)$ ; the problem was to trace the distribution of these radicles. The substance is very feebly basic, crystallises from glacial acetic acid in the free state, and does not form salts with acids in aqueous solutions. When nitrous acid acts on it in glacial acetic acid, a nitrite is produced which is easily decomposed by aqueous alkalis regenerating the base. It appears to be a base containing only tertiary nitrogen. This condition would be satisfied if each nitrogen atom were attached to a methylene radicle. When the base is heated with hydriodic acid and red phosphorus in sealed tubes at  $180^\circ$ , it is found that two methylene radicles and one atom of nitrogen are eliminated, and that naphthacridine is produced. This indicates that the third methylene group was directly attached to both the naphthalene nuclei, and accordingly the formula of the original base is best expressed in the following manner.



The first action in the sealed tube experiment is probably one of hydrolysis,



This diamine is not isolated as such, but undergoes condensation in accordance with the following equation.



The ammonia is eliminated in theoretical quantity, and the yield of naphthacridine is not less than 69 per cent. The formaldehyde which should be formed could not be detected, but it was scarcely to be expected that it would remain unchanged under the conditions of the experiment.

If this explanation of the experimental results is correct, the base  $C_{23}H_{18}N_2$  should be called dimethylenediaminodinaphthylmethane.

The fourth substance obtained by the action of formaldehyde on  $\beta$ -naphthylamine is formed according to this equation,



but has hitherto only been obtained in small quantity, the yield being about 2 or 3 per cent. Its complete analysis gives the empirical formula  $C_{11}H_8N$ , and the analysis of its salts indicates that it is a monacidic base having the molecular formula  $C_{22}H_{16}N_2$ . The nitrite, which is produced by adding sodium nitrite to its glacial acetic acid solution, has the formula  $C_{22}H_{16}N_2 \cdot HNO_2$ , and again yields the base on treatment with aqueous alkalis. It appears, therefore, to be a tertiary base, but a more detailed investigation of its constitution will only be possible when a larger amount of the substance is available.

#### EXPERIMENTAL.

##### *Action of Formaldehyde on $\beta$ -Naphthylamine in Acidified Alcoholic Solution.*

One hundred and forty-three grams of  $\beta$ -naphthylamine (1 mol.) were dissolved in 400 grams of alcohol, and 80 grams of 40 per cent. formaldehyde (1 mol.) were added to the warm alcoholic solution; the liquid became turbid and a heavy brown oil separated. On adding 37 grams of concentrated hydrochloric acid ( $\frac{1}{3}$  mol.) slowly, the oily layer disappeared, and the clear solution, which was at first reddish-brown, on being heated on the water bath, changed to green. After boiling for half an hour, a yellow, granular precipitate appeared and rapidly increased in quantity until the contents of the flask became almost solid, and at the same time an ammoniacal gas was evolved. This was collected in hydrochloric acid and the platinumchloride prepared, which, on analysis, proved to be the ammonium salt.

0.1334 gave 0.0582 Pt. Pt = 43.63.

0.0982 „ 0.0429 Pt. Pt = 43.68.

$(NH_4)_2PtCl_6$  requires Pt = 43.80 per cent.

The yellow precipitate, after being collected and washed four times with hot alcohol to remove some tarry impurity, was dissolved in benzene and the solution allowed to crystallise, when orange-coloured needles were obtained. A portion of this was again crystallised from benzene, and then twice from alcohol, in which solvent it is only sparingly soluble; it then melted at 225—226°, sintering together at about 221°.

0.1387 gave 0.4598  $CO_2$  and 0.0618  $HO_2$ . C = 90.41; H = 4.94.

0.2264 „ 9.5 c.c. moist N at 20° and 768.5 mm. N = 4.85.

$C_{21}H_{13}N$  requires C = 90.32; H = 4.66; N = 5.02 per cent.

The benzene mother liquor gave another crop of orange-coloured needles on standing for several days. The filtrate was then considerably concentrated, from 2 litres to about 250 c.c., when it deposited



a mass of pale yellow crystals melting at about  $192^{\circ}$ . This product, dissolved in ethylic acetate and allowed to evaporate spontaneously, yielded successive crops of mixed crystals containing two dissimilar kinds; the predominant substance crystallised in irregular clusters of short, colourless prisms melting at  $202\text{--}203^{\circ}$ , whilst the substance occurring in smaller quantity crystallised in amber-coloured prisms of a more acicular habit. The latter, on being picked out and recrystallised from alcohol, finally yielded straw-coloured needles melting at  $216^{\circ}$ . These properties identified the substance as Reed's naphth-acridine. The substance melting at  $202\text{--}203^{\circ}$ , when twice recrystallised from ethylic acetate, was obtained in well-defined, colourless prisms often exhibiting cruciform twinning.

0.1271 gave  $0.3984\text{ CO}_2$  and  $0.0664\text{ H}_2\text{O}$ .  $\text{C} = 85.48$ ;  $\text{H} = 5.80$ .

0.3122 ,,  $23.2\text{ c.c.}$  moist nitrogen at  $18.6^{\circ}$  and  $769\text{ mm.}$   $\text{N} = 8.66$ .

$\text{C}_{23}\text{H}_{18}\text{N}_2$  requires  $\text{C} = 85.71$ ;  $\text{H} = 5.59$ ;  $\text{N} = 8.70$  per cent.

The alcoholic mother liquor from the original yellow precipitate, when distilled on the water bath as long as alcohol came over, left a residue which separated into two layers, namely, an upper, aqueous layer which was found to contain only ammonium chloride and a little resinous matter, and a lower, brown, tarry mass which partially solidified on cooling. The latter was boiled with aqueous alkalis to decompose any chlorides which might be present, then extracted with benzene, petroleum carefully added to the benzene solution, and the clear solution decanted from the tarry substance which separated; on now adding more petroleum, a substance crystallising in rosettes of small, yellow needles appeared on the sides of the beaker. This, after being collected and freed from admixed tar by washing with a little cold alcohol, was crystallised from the latter; when pure, it is only sparingly soluble in alcohol. For the purpose of analysis, it was recrystallised repeatedly from ethylic acetate, from which it separates in tufts of woolly needles melting at  $186\text{--}187^{\circ}$ .

0.1297 gave  $0.4055\text{ CO}_2$  and  $0.0617\text{ H}_2\text{O}$ .  $\text{C} = 85.27$ ;  $\text{H} = 5.28$ .

0.1639 ,,  $0.5144\text{ CO}_2$  ,,  $0.0766\text{ H}_2\text{O}$ .  $\text{C} = 85.60$ ;  $\text{H} = 5.19$ .

0.1699 ,,  $13.60\text{ c.c.}$  moist nitrogen at  $17.5^{\circ}$  and  $768\text{ mm.}$   $\text{N} = 9.37$ .

0.1342 ,,  $10.6\text{ c.c.}$  ,, ,,  $16^{\circ}$  ,,  $755\text{ mm.}$   $\text{N} = 9.15$ .

$(\text{C}_{11}\text{H}_5\text{N})_2$  requires  $\text{C} = 85.71$ ;  $\text{H} = 5.19$ ;  $\text{N} = 9.05$  per cent.

In this experiment, the total weight of recrystallised products was about 86 grams, and was made up as follows: Isonaphthacridine, orange base, 35 grams; naphthacridine, 7 grams;  $\text{C}_{23}\text{H}_{18}\text{N}_2$ , 41 grams; and 3.5 of  $\text{C}_{22}\text{H}_{16}\text{N}_2$ .

Another series of experiments was made, using the same quantities as in the one described above, but in which the hydrochloric acid was added before the formaldehyde. The reaction in this case was more

violent, no separation of heavy oil occurred, and after one-fourth of the aldehyde had been added the whole turned green and became nearly solid, with considerable development of heat. The rest of the aldehyde was added more rapidly, when the whole mass became yellow, and after boiling for 2 hours the precipitate was collected and recrystallised from benzene as in the preceding experiment. The yield of isonaphthacridine obtained by this method was larger than in the previous experiment, 70 to 80 grams being usually obtained, and the amount of the base,  $C_{23}H_{18}N_2$ , was less, usually about 18 grams. The amounts of naphthacridine and of the base,  $C_{22}H_{16}N_2$ , remain about the same.

Lastly, the effect of using a larger quantity of formaldehyde was investigated. One hundred and forty-three grams of  $\beta$ -naphthylamine were dissolved in 500 grams of alcohol and 120 grams ( $1\frac{1}{2}$  mols.) of formaldehyde were gradually added. The first 60 grams appeared to react energetically, a turbidity was produced, and a large quantity of heavy brown oil separated, but very little action accompanied the addition of the remainder of the aldehyde. Sixty-three grams of concentrated hydrochloric acid were now slowly added, when the oily layer disappeared, the solution being a deep reddish-brown. After heating on the water bath for 45 minutes, a yellowish-green precipitate appeared; the heating was continued for another hour, and the precipitate was collected and washed with hot alcohol. This precipitate weighed 25 grams. The filtrate, on standing 2 days, deposited a brownish-yellow, tarry precipitate which weighed about 47 grams. In this experiment, therefore, more than half the product of reaction remains in the alcoholic mother liquor; this was distilled until all the alcohol was driven off. The aqueous portion of the residue contained ammonium chloride, and the pitchy residue, separated from the aqueous portion, weighed about 100 grams.

The first precipitate, which owed its green colour to the presence of a small quantity of isonaphthacridine hydrochloride, was boiled with alcoholic ammonia to decompose any hydrochlorides, and then dissolved in alcohol. The solution yielded a crop of crystals melting at  $176-177^\circ$ , but these were found to consist of a mixture of the base,  $C_{23}H_{18}N_2$ , crystallising in semi-opaque, colourless prisms giving the correct melting point  $202-203^\circ$ , and naphthacridine crystallising in amber-coloured prisms melting at  $214-215^\circ$ . A mixture of the purified substances melted at  $169-170^\circ$ , which is nearly the same as the melting point of the mixed crystals obtained in this experiment.

The second precipitate (47 grams) was extracted successively with hot water, hydrochloric acid, and a little alcohol; the residue appeared to consist almost entirely of the base  $C_{23}H_{18}N_2$ , and when recrystallised

from glacial acetic acid melted at 201—202° (correct m. p., 202—203°), the weight obtained being 22 grams.

The residue (100 grams) was likewise extracted with hot water, hydrochloric acid, and alcohol, and the almost white product, on recrystallisation from acetic acid, gave 60 grams of the base  $C_{23}H_{18}N_2$ .

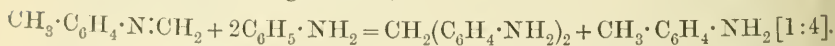
The aqueous and hydrochloric acid extracts were mixed and neutralised with sodium carbonate, and the pale yellow precipitate collected, and recrystallised from alcohol, and then from ethylic acetate, when it separated in tufts of woolly needles melting at 186—187°, and was identical with the base,  $C_{22}H_{16}N_2$ , obtained in the former experiment. When formaldehyde is in excess, the chief product is the substance  $C_{23}H_{18}N$ , and in this experiment 100 grams of the recrystallised base were obtained, together with 5 grams of naphthacridine, a small quantity of isonaphthacridine, and 3 to 4 grams of the base  $C_{22}H_{16}N_2$ .

About 20 grams of tarry matter were also formed, from which nothing definite could be extracted. In these experiments, great difficulty was experienced in separating naphthacridine from the base,  $C_{23}H_{18}N_2$ , for they crystallise together from their solutions in alcohol, acetone, ethylic acetate, and benzene, and from glacial acetic acid the acetate of naphthacridine separates along with the free base,  $C_{23}H_{18}N_2$ . Further experiments have shown that they can both be obtained with great ease by reactions which yield them as the sole products.

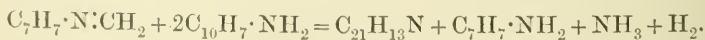
#### *Isonaphthacridine, $C_{21}H_{13}N$ .*

The analysis of the orange base,  $C_{21}H_{13}N$  (page 541), indicates that it is isomeric with Reed's naphthacridine, and it has been found possible to prepare it by a method not involving the use of acids, or of any solvent which might convert any portion of it into the latter base.

Meister, Lucius, and Brüning (D.R.P., 53937, 1889) employ anhydroformaldehyde-paratoluidine as a carrier of the methylene group in the formation of diphenylmethane derivatives, for example, when aniline is heated with it, diamidodiphenylmethane is produced and paratoluidine is regenerated,



When this reagent is heated with  $\beta$ -naphthylamine, the chief product is isonaphthacridine; in this case, ammonia and hydrogen are eliminated.



The hydrogen probably acts destructively on a portion of the reacting materials, for some tarry matter is always produced, and the yield is only about 44 per cent. of the theoretical.

Seventy grams of  $\beta$ -naphthylamine were melted with 35 grams

of anhydroformaldehyde-paratoluidine, and the fused mass kept at  $170-180^{\circ}$  until the evolution of ammonia had ceased. The brownish-yellow melt after being broken up into small pieces, was steam distilled until all the paratoluidine and some of the  $\beta$ -naphthylamine had passed over into the distillate, and the residue, freed from the remaining  $\beta$ -naphthylamine by repeated extractions with hot water, was recrystallised from benzene; the weight of crystallised isonaphthacridine obtained was 30 grams. The filtrate, on concentration, deposited nacreous plates, which, after recrystallisation from ethylic acetate, melted at  $169^{\circ}$ . A small portion mixed with a little pure  $\beta\beta$ -dinaphthylamine also gave this melting point, thus identifying the substance with this base. The mother liquor from the dinaphthylamine deposited a brown substance, which, on crystallisation from alcohol, melted at  $175^{\circ}$ . The addition of petroleum to the benzene filtrate caused the separation of a tarry oil, and on adding more petroleum to the clear solution a semi-solid, brown mass separated at the bottom of the beaker, and after some time a brownish-yellow deposit formed on the sides; on recrystallisation from alcohol, this yielded a substance melting at about  $175^{\circ}$ , which was added to the former crop melting at this temperature, and the whole recrystallised several times from alcohol, when 1.8 grams of a pale yellow substance melting at  $178-179^{\circ}$  were obtained.

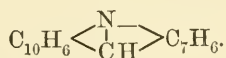
This compound crystallises well from alcohol in fine, asbestos-like needles, which spread through the whole bulk of the solution, and show no tendency to cling to the sides of the crystallising vessel. When collected, these shrink together, forming a closely felted mass of a pale yellow colour. The solution in alcohol exhibits a reddish-violet fluorescence like that of naphthacridine.

0.1230 gave 0.3984  $\text{CO}_2$  and 0.0590  $\text{H}_2\text{O}$ .  $\text{C} = 88.33$ ;  $\text{H} = 5.33$ .

0.1680 „ 8.7 c.c. moist N at  $19^{\circ}$  and 775 mm.  $\text{N} = 6.08$ .

$\text{C}_{18}\text{H}_{13}\text{N}$  requires  $\text{C} = 88.88$ ;  $\text{H} = 5.35$ ;  $\text{N} = 5.76$  per cent.

The results of analysis indicate that the substance is probably a tolyl analogue of naphthacridine of the formula,



The alcoholic filtrates from the recrystallisation yielded very small quantities of naphthacridine and of the base  $\text{C}_{22}\text{H}_{18}\text{N}_2$ . A quantity of tarry matter was also produced in this reaction, from which nothing definite could be extracted. A portion of the isonaphthacridine, after being thrice recrystallised from benzene, melted at  $225-226^{\circ}$ , sintering together before melting at  $221^{\circ}$ .



0.0987 gave 0.3254  $\text{CO}_2$  and 0.0442  $\text{H}_2\text{O}$ . C = 89.92; H = 4.97.  
 0.1907 „ 0.6291  $\text{CO}_2$  „ 0.0873  $\text{H}_2\text{O}$ . C = 89.97; H = 5.09.  
 0.1495 „ 7 c.c. moist nitrogen at  $24^\circ$  and 764 mm. N = 5.28.  
 $\text{C}_{21}\text{H}_{13}\text{N}$  requires C = 90.32; H = 4.66; N = 5.02 per cent.

The remainder of the 30 grams obtained in this operation were recrystallised six times from benzene, but no alteration in the melting point or in the colour of the substance was noticeable. It crystallises from benzene in beautiful, orange needles, and the solution exhibits a reddish-violet fluorescence. When a portion is sealed up with benzene and heated until it has all dissolved and the solution allowed to cool slowly, lath-like, orange crystals are obtained over half an inch long. The compound is sparingly soluble in alcohol, one part dissolving in about 300 of the hot solvent, but it is almost insoluble in the cold. It is three times as soluble in amyl alcohol as in ethyl alcohol, and separates from both these solvents as a felted mass of fine orange needles.

When the base is triturated with strong hydrochloric acid, an insoluble green hydrochloride is produced. Some of the hydrochloride prepared in this way, after being washed with cold alcohol and ether, was dried over quicklime in a partially exhausted desiccator and analysed; chlorine determinations made with this specimen indicated that the combination with hydrogen chloride in aqueous solution was incomplete, the percentage of chlorine being lower than that required for the monhydrochloride. 0.6035 gram of the base was subjected to the action of the dry gas, when the base turned green, and the tube containing it became perceptibly warm; a stream of dry air was then drawn through the tube for several hours to remove the excess of hydrogen chloride, and the weight of hydrochloride then obtained was 0.6754 gram. This corresponds with an addition of 10.64 per cent. of hydrogen chloride, the value calculated for the monhydrochloride,  $\text{C}_{21}\text{H}_{13}\text{N}, \text{HCl}$ , being 11.5.

#### *Conversion of Isonaphthacridine into Naphthacridine.*

On passing dry hydrogen chloride into isonaphthacridine dissolved in dry benzene, a yellow hydrochloride was precipitated which was collected, washed with dry benzene and dry ether, dried at  $110^\circ$ , and analysed.

0.2349 gave 0.1074  $\Delta\text{gCl}$ . Cl = 11.31.  
 0.2220 „ 8.8 c.c. moist nitrogen at  $20^\circ$  and 760 mm. N = 4.53.  
 $\text{C}_{21}\text{H}_{13}\text{N}, \text{HCl}$ , requires Cl = 11.25; N = 4.43 per cent.



On treating this salt with aqueous alkalis, naphthacridine melting at  $216^{\circ}$ , and not isonaphthacridine, was obtained, which on treatment with hydrochloric acid again furnished the yellow hydrochloride.

1.2450 grams of isonaphthacridine, recrystallised six times from benzene, were dissolved in about 50 c.c. of glacial acetic acid, and dry hydrogen chloride passed into the warm solution; the hydrochloride which came down at first had a green tinge, but eventually became yellow; it was collected in a Gooch crucible, washed with glacial acetic acid and dry ether, dried at  $110-120^{\circ}$ , and weighed; 1.397 grams were obtained, the theoretical quantity being 1.4086 grams. The base, liberated by warming the salt with ammonia, was pale yellow and melted at  $213-214^{\circ}$  (naphthacridine melts at  $216^{\circ}$ ); it was then recrystallised from alcohol, and the first crop of crystals weighed 1.12 grams and melted at  $215^{\circ}$ , and when mixed with pure naphthacridine there was no depression in the melting point.

0.1676 gave 0.5546  $\text{CO}_2$  and 0.0723  $\text{H}_2\text{O}$ .  $\text{C} = 90.23$ ;  $\text{H} = 4.79$ .

$\text{C}_{21}\text{H}_{13}\text{N}$  requires  $\text{C} = 90.32$ ;  $\text{H} = 4.66$  per cent.

#### *Action of Solvents on Isonaphthacridine.*

Isonaphthacridine is far less soluble in ordinary solvents than naphthacridine. The alcoholic mother liquors from the recrystallisation of isonaphthacridine slowly deposit amber-coloured prisms of naphthacridine; 1.5 grams of recrystallised isonaphthacridine, heated with acetone for several hours, on cooling, deposited 0.6 gram of naphthacridine (m. p.  $216^{\circ}$ ) in clear, amber-coloured prisms.

One gram of isonaphthacridine, after six crystallisations from benzene, was boiled for 5 days with just sufficient acetone to keep it in solution when boiling; the quantity of orange needles separating was less each morning, until at the end of that time the crystals were no longer of this form, but appeared as amber-coloured prisms. The acetone was distilled off, and the residue recrystallised from alcohol, when 0.65 gram of naphthacridine was obtained in the first crop of crystals, which only gave the yellow hydrochloride; the filtrate, on evaporation, gave a residue which gave a greenish-yellow hydrochloride, indicating that the conversion was not quite complete.

When isonaphthacridine is dissolved in hot glacial acetic acid, and the solution quickly cooled, its acetate separates in rosettes of green needles, but when the solution is boiled for some time, the yellow acetate of naphthacridine crystallises out on cooling.

Isonaphthacridine appears to be a tertiary base; when treated with benzoic chloride by the Schotten-Baumann method, it remains unchanged, but when boiled for some time with acetic anhydride, it is converted into naphthacridine, which crystallises out in amber-coloured prisms. When

sodium nitrite is added to its solution in glacial acetic acid, a brownish-yellow substance is obtained insoluble in the ordinary solvents, but soluble in aniline, from which it crystallises in yellow needles; this is an unstable nitrite of naphthacridine, for on digesting it with cold alcohol (90 per cent.) it is decomposed, yielding naphthacridine. As a proof that all the nitrous acid had been removed by this treatment, the nitrogen was determined in the naphthacridine so produced.

0.2772 gave 11.5 c.c. moist nitrogen at 22° and 764 mm.  $N = 4.72$ .

$C_{21}H_{13}N$  requires  $N = 5.02$  per cent.

#### *Action of Alkyl Iodides on Isonaphthacridine.*

Isonaphthacridine was heated with excess of methylic iodide in sealed tubes at 140°; the yellow *methiodide* produced was insoluble in the ordinary solvents, but crystallised from aniline in small, golden-yellow plates, decomposing somewhat indefinitely at 262—264°.

0.1368 gave 0.0775 AgI.  $I = 30.60$ .

$C_{21}H_{13}NCH_3I$  requires  $I = 30.08$  per cent.

The *ethiodide* was similarly prepared, and crystallises from aniline in short, orange-yellow prisms melting at 283—284°.

0.1148 gave 0.0606 AgI.  $I = 28.52$ .

$C_{21}H_{13}N \cdot C_2H_5I$  requires  $I = 29.04$  per cent.

Both these substances are derivatives of naphthacridine, for on treating them with alcoholic ammonia, or even on digesting them with undried ether, this base is liberated.

#### *Naphthacridine.*

Reed's method of preparation was repeated. A mixture of 33 grams of methylal with 30 grams of acetone was saturated with hydrogen chloride at 10°, and then added to a mixture of 65 grams of  $\beta$ -naphthylamine and 200 grams of concentrated hydrochloric acid; the temperature rose considerably, and the mixture at once became brown. After being allowed to remain overnight, it was heated for 5 hours on the water bath, and then poured into an excess of caustic soda solution; ammonia was evolved, and a brown, tarry mass was obtained, which was extracted with hot water to remove  $\beta$ -naphthylamine, and then with ether to remove some of the oily impurity. The residue was dissolved in acetone, and the solution treated with alcoholic picric acid solution as in Reed's experiment (*loc. cit.*). The first crop of picrate yielded impure naphthacridine which required many recrystallisations before its melting point remained constant at 216°, the second crop of

picrate, obtained after distilling over two-thirds of the acetone, yielded the base  $C_{23}H_{18}N_2$ , which was purified by recrystallisation from ethylic acetate.

In Reed's second method, naphthacridine was obtained by the action of methylal alone on  $\beta$ -naphthylamine; this experiment was repeated, using the proportions employed by Reed. As the mixture of methylal and  $\beta$ -naphthylamine hydrochloride in excess of hydrochloric acid was heated to  $100^\circ$ , it was observed that at a certain stage it became yellowish-green, and on further heating changed to yellow; this change indicates the formation of isonaphthacridine as an intermediate product, and its subsequent conversion into naphthacridine. The mixture was made alkaline with caustic soda, the  $\beta$ -naphthylamine removed by hot water, and the residue dissolved in alcohol; the alcoholic solution deposited light yellow needles mixed with a brown impurity. The whole deposit was again boiled with alcohol until the greater portion had dissolved, and the residue crystallised from ethylic acetate, when the base  $C_{23}H_{18}N_2$  was obtained, melting at  $203^\circ$  and crystallising in its very characteristic manner, in colourless prisms.

The alcoholic mother liquor yielded impure naphthacridine which was only obtained pure after a tedious series of recrystallisations.

Naphthacridine is most easily prepared from isonaphthacridine, as the latter is quantitatively converted into it. It is merely necessary to dissolve isonaphthacridine in glacial acetic acid heated to boiling for 6 or 7 hours, and allow the solution to cool, when brownish-yellow crystals of naphthacridine acetate separate. These, after being collected and washed with acetic acid and alcohol, are decomposed by ammonia solution; the naphthacridine thus obtained, after two crystallisations from alcohol, is quite pure, and crystallises in beautiful, straw-coloured needles melting at  $216^\circ$ .

0.1384 gave 0.4568  $CO_2$  and 0.0585  $H_2O$ .  $C = 90.03$ ;  $H = 4.68$ .

$C_{21}H_{13}N$  requires  $C = 90.32$ ;  $H = 4.66$  per cent.

Naphthacridine appears to crystallise in two forms; from its concentrated solution in alcohol, it separates quickly as straw-coloured needles, but when allowed to crystallise more slowly from its solution in alcohol, ethylic acetate, acetone, or benzene, it forms clear, amber-coloured prisms, which become opaque on drying at  $100^\circ$ . Both forms have the same melting point, and give the yellow hydrochloride.

The determination of the molecular weight of naphthacridine was made by the freezing point method.

0.2155 in 17.46 benzene gave a depression of  $0.226^\circ$ .

$M = 280$ ;  $C_{21}H_{13}N = 279$ .

The molecular weight of isonaphthacridine could not be obtained in this way, owing to its great insolubility in cold benzene.

Naphthacridine, heated with methylic iodide in sealed tubes at  $140^{\circ}$ , gives a yellow methiodide insoluble in all low boiling point solvents, which crystallises from aniline in golden-yellow scales decomposing near  $263^{\circ}$ , and is identical with that obtained by the action of methylic iodide on isonaphthacridine.

0.0973 gave 0.0550 AgI.  $I = 30.54$ .

$C_{21}H_{13}NCH_3I$  requires  $I = 30.08$ .

The ethiodide prepared in a similar manner is identical with that from isonaphthacridine; it crystallises from aniline in orange-yellow prisms, and decomposes at  $282-283^{\circ}$ .

0.1160 gave 0.0637 AgI.  $I = 29.66$ .

$C_{21}H_{13}N \cdot C_2H_5I$  requires  $I = 29.04$ .

In studying the products of the hydrogenation of isonaphthacridine and naphthacridine by the action of sodium and amylic alcohol, it was noticed that both compounds yielded a substance crystallising in red needles, which is being further investigated; isonaphthacridine also appeared to remain partly unacted on, whilst naphthacridine, under similar conditions, gave a certain quantity of isonaphthacridine. An experiment was therefore made with a view to determine whether naphthacridine could be reconverted into isonaphthacridine by the action of sodium amyloxide. Five grams of naphthacridine were dissolved in 100 grams of amylic alcohol, mixed with 60 grams of amylic alcohol in which 7 grams of sodium had been dissolved, and the mixture heated for 24 hours. The amylic alcohol was then driven off by steam distillation, and the residue dried and dissolved in benzene. A crop of orange needles separated which weighed 2 grams; these did not melt at  $216^{\circ}$ , but at  $225-226^{\circ}$ , and yielded the green hydrochloride. The filtrate contained a mixture of isonaphthacridine and naphthacridine, and it has not been found possible to make this conversion complete.

#### *The Base $C_{23}H_{18}N_2$ .*

This base is obtained by the action of methylal or of formaldehyde on  $\beta$ -naphthylamine in the presence of hydrochloric acid.

*Action of Formaldehyde on  $\beta$ -Naphthylamine in Glacial Acetic Acid.*—Seventy-two grams of  $\beta$ -naphthylamine were dissolved in 250 grams of glacial acetic acid, the solution cooled to  $3^{\circ}$ , and 60 grams of 40 per cent. formaldehyde solution\* ( $1\frac{1}{2}$  mols.) slowly added with con-

\* Although the formaldehyde solution employed in these experiments gave no indications of acetone when submitted to the tests for this substance, an experiment was made with a sample of formaldehyde solution prepared from pure methylic alcohol



stant stirring. A white, amorphous precipitate separated until the mixture acquired a pasty consistency, but, on standing for about an hour, the precipitate redissolved, and the clear liquid was decanted from a slight amount of tar which remained insoluble. A crystalline precipitate then gradually separated; this was filtered off, and alcohol added to the filtrate, and the whole heated to boiling; on cooling, a second crop was obtained; on pouring the mother liquor into a large quantity of water, a resinous mass separated, which, after being extracted with a little alcohol, became granular and crystalline. The entire crystalline product weighed 68 grams, and was purified by recrystallisation from glacial acetic acid, when it melted at  $202-203^{\circ}$ . The crystals may be obtained colourless by boiling the acetic acid solution with a little zinc dust.

A portion, after four crystallisations from alcohol, gave the following numbers on analysis.

0.1364	gave	0.4312 $\text{CO}_2$	and	0.0694 $\text{H}_2\text{O}$ .	$\text{C} = 86.21$ ; $\text{H} = 5.65$ .
0.1409	„	0.4437 $\text{CO}_2$	„	0.0721 $\text{H}_2\text{O}$ .	$\text{C} = 85.87$ ; $\text{H} = 5.68$ .
0.1128	„	0.3549 $\text{CO}_2$	„	0.0576 $\text{H}_2\text{O}$ .	$\text{C} = 85.81$ ; $\text{H} = 5.67$ .
0.2040	„	16.2 c.c. moist N	at $24.5^{\circ}$ and 766 mm.	$\text{N} = 8.95$ .	

An analysis of this base made from formaldehyde and  $\beta$ -naphthylamine in alcoholic solution gave the following.

0.1328	gave	0.4172 $\text{CO}_2$	and	0.0691 $\text{H}_2\text{O}$ .	$\text{C} = 85.68$ ; $\text{H} = 5.80$ .
0.3200	„	23.4 c.c. moist N	at $16.5^{\circ}$ and 768.5 mm.	$\text{N} = 8.62$ .	

The mean of these analyses including those of page 542, gave the following values.

$\text{C} = 85.81$  ;  $\text{H} = 5.72$  ;  $\text{N} = 8.77$  per cent.

$\text{C}_{23}\text{H}_{18}\text{N}_2$  requires  $\text{C} = 85.71$  ;  $\text{H} = 5.59$  ;  $\text{N} = 8.70$ .

$\text{C}_{24}\text{H}_{20}\text{N}_2$  „  $\text{C} = 85.71$  ;  $\text{H} = 5.95$  ;  $\text{N} = 8.33$ .

A molecular weight determination by the freezing point method gave the following results.

0.4106 in 18.87 benzene gave a depression of  $0.340^{\circ}$ .  $\text{M} = 326$ .

0.1660 „ 26.84 „ „ „  $0.099^{\circ}$ .  $\text{M} = 320$ .

$\text{C}_{23}\text{H}_{18}\text{N}_2 = 322$  ;  $\text{C}_{24}\text{H}_{20}\text{N}_2 = 336$ .

In preparing the base by the method just described, the solution must be kept quite cold during the addition of the formaldehyde, otherwise the temperature rises very rapidly to  $40^{\circ}$  or  $50^{\circ}$ , the solution turns green, and a large amount of tarry matter is produced, from

which was kindly placed at my disposal by Messrs. Mercklin and Lösekann, of Hanover. As the base melting at  $203^{\circ}$  was obtained equally readily under these conditions, there can be no doubt that acetone plays no part in the condensation.



which the base cannot be obtained. One quantity which had been spoiled in this way was examined, in order to see whether any definite product could be isolated. For this purpose, the green, tarry mass was extracted with benzene, to which sodium carbonate was added, in order to decompose any acetates which might be contained in the tar. The benzene solution deposited orange needles of isonaphthacridine, the yield being about 10 per cent. on the amount of  $\beta$ -naphthylamine employed.

The base  $C_{23}H_{18}N_2$  is readily soluble in acetic acid, benzene, amyl alcohol, and ethylic acetate, sparingly in ethylic alcohol and in ether, crystallising from these solvents in colourless, transparent prisms often showing cruciform twinning.

It remains unchanged under the influence of reducing agents, zinc dust and acetic acid being without action on it, and the greater part of the substance is recovered when subjected to the action of sodium and amyl alcohol. A strong aqueous solution of sodium nitrite, when added to an acetic acid solution of the base, precipitates a colourless nitrite which is decomposed into the base and nitrous acid, even on agitation with moist ether. The non-formation of a nitrosamine or of a diazo-salt in this experiment points to the conclusion that the base contains only tertiary nitrogen.

When heated with strong hydrochloric acid at  $180^\circ$ , only ammonium chloride and a black, tarry mass are obtained, whilst at lower temperatures the base remains unaltered.

#### *Conversion of the Base $C_{23}H_{18}N_2$ into Naphthacridine.*

Forty grams of the base were sealed up with 8 grams of red phosphorus and 60 grams of strong hydriodic acid (sp. gr. 1.94) and heated for 5 to 6 hours at  $180^\circ$ . The tubes were found to contain a small quantity of permanent gas which contained phosphine, an aqueous, strongly acid layer, a small quantity of an oil lighter than water and having a penetrating odour, and a brown, resinous mass. The liquid portions were poured off from the resinous product and steam distilled, when the oil passed over with the distillate. This was shaken up with ether, and on distilling off the solvent only about 0.5 c.c. of oil was left. The whole quantity obtained from two series of experiments, when distilled, boiled between  $205^\circ$  and  $215^\circ$ ; its solution in chloroform slowly decolorised bromine, with evolution of hydrogen bromide. These properties resemble those of the di- and tetra-hydronaphthalenes, but the amount obtained was so small that the substance was not further investigated.

The aqueous solution left in the distilling flask after removal of the oil was made alkaline with soda and distilled; ammonia was evolved,

and on being collected in hydrochloric acid and evaporated to dryness, weighed 6.2 grams. The quantity which should have been obtained, supposing that half the nitrogen was eliminated as ammonia, is 6.4 grams.

The resinous portion was found to be insoluble in all the low boiling point solvents, but it dissolved in aniline, and the solution on cooling deposited bronzy-yellow flakes which were collected and dried on porous plates; 35 grams of the recrystallised substance were obtained. This substance proved to be the hydriodide of naphthacridine, and the yield of recrystallised product was 69 per cent. of the theoretical.

After three crystallisations from freshly distilled aniline, followed by extraction with dry ether in order to remove the solvent as far as possible, a specimen gave the following numbers.

0.1316 gave 0.0741 AgI.  $I = 30.41$ .

0.1344 „ 0.0759 AgI.  $I = 30.51$ .

$C_{21}H_{13}N, HI$  requires  $I = 31.11$  per cent.

The naphthacridine obtained from the hydriodide by warming it with alcoholic potash, after repeated crystallisation from alcohol, melted at  $214-215^\circ$ , and the melting point remained unaltered when mixed with pure naphthacridine (m. p.  $216^\circ$ ).

0.1593 gave 0.5314  $CO_2$  and 0.0690  $H_2O$ .  $C = 90.41$ ;  $H = 4.81$ .

$C_{21}H_{13}N$  requires  $C = 90.32$ ;  $H = 4.66$  per cent.

The result throws considerable light on the constitution of the base  $C_{23}H_{15}N_2$ ; one of the methylene radicles must be directly attached to the two naphthalene nuclei, and since the base is a tertiary one, the other two are probably attached to the two nitrogen atoms.

The formula of the substance may be written in the following manner,  $CH_2(C_{10}H_6N:CH_2)_2$ . An explanation of the reaction with hydriodic acid and red phosphorus, and the graphical formula of the substance, are given in the theoretical part of the paper.

Although this is such a beautifully crystalline substance, it does not yield well-defined crystalline derivatives. It is sulphonated when treated at  $100^\circ$  with sulphuric acid containing a little sulphur trioxide, but the free sulphonic acid forms a gelatinous mass and its barium and potassium salts are devoid of any tendency to crystallise. The action of bromine or nitric acid gives rise to indefinite insoluble products.

*The Base  $C_{22}H_{16}N_2$ , melting at  $186-187^\circ$ .*

This is the substance which is formed in small amount (about 2 per cent.) when formaldehyde reacts with an alcoholic solution of  $\beta$ -naphthylamine in the presence of hydrochloric acid.

Its complete analysis (page 542) has indicated the empirical formula

$C_{11}H_8N$ . Its hydrochloride, prepared by dissolving the base in alcoholic hydrochloric acid, is deposited in tufts of fine, white needles melting indefinitely at  $255^\circ$ .

0.1398 gave 0.0566 AgCl. Cl = 10.01.

$C_{22}H_{16}N_2 \cdot HCl$  requires Cl = 10.30 per cent.

The base is fairly soluble in hot alcohol, but almost insoluble in the cold, and readily soluble in ethylic acetate or acetone, from which it crystallises in tufts of fine, pale-yellow needles. It is sparingly soluble in hot water, and dissolves readily in benzene, from which it is precipitated by light petroleum. It is exceedingly soluble in cold glacial acetic acid, and when sodium nitrite is added to this solution a copious white precipitate, consisting of the nitrite, separates in rosettes of small, colourless needles. A nitrogen determination of the substance gave the following.

0.1257 gave 12.9 c.c. moist nitrogen at  $14^\circ$  and 761 mm. N = 12.10.

$C_{22}H_{16}N_2 \cdot HNO_2$  requires N = 11.83 per cent.

The base is regenerated from the nitrite on treatment with aqueous soda. When treated with hydriodic acid in the cold, it gives a blue precipitate, and when heated with this acid and red phosphorus at  $180^\circ$ , no definite product is obtained and no nitrogen is eliminated as ammonia.

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## LVII.—*Action of Hydrogen Bromide in Presence of Ether on Carbohydrates and certain Organic Acids.*

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It has been shown by one of the authors (Trans., 1896, 553) that the ethylic salt of dihydroxymaleic acid can readily be obtained by the interaction of the free acid with anhydrous ethylic ether in presence of dry hydrogen bromide at the ordinary temperature. The product is identical in every respect with that obtained from the acid and ethylic alcohol in presence of hydrogen chloride, and the yield appears to be about the same. A similar result cannot be effected by substituting hydrogen chloride for hydrogen bromide. Ethylic ether is known, of course, to react with sulphuric, hydrochloric, and a few other inorganic acids, under certain conditions, to form ethylic salts, but no such behaviour towards organic acids appears to have been observed.

It was therefore considered advisable to extend the observations to some other acids, in order to ascertain whether the reaction is one of general application. Accordingly, experiments were made with oxalic, acetic, benzoic, stearic, and boric acids. In every case examined, the ethylic salt of the acid was readily obtained, the yield being generally good.

The acid was in each case covered with anhydrous ether purified carefully from alcohol and water as previously described, dry hydrogen bromide was passed into the mixture until it was saturated or nearly saturated, and it was then left for some days. The product was separated and purified by the ordinary methods.

*Oxalic Acid.*—Twenty grams of the pure dry acid were covered with about 200 c.c. of ether, saturated with dry hydrogen bromide, and after three days the mixture was treated with water; the heavy liquid which separated was purified by washing with dilute sodium carbonate solution, dried over calcium chloride, and distilled. The portion distilling between  $178^{\circ}$  and  $182^{\circ}$  weighed 15 grams, and had all the properties of ethylic oxalate, as recognised by its boiling point, odour, action on aqueous ammonia, and action on alcoholic potash.

*Acetic Acid.*—Twenty grams of glacial acetic acid were covered with about 150 c.c. of ether and saturated with dry hydrogen bromide; after three days, it was treated in exactly the same way as the ethylic oxalate. The portion distilling between  $75^{\circ}$  and  $82^{\circ}$  was collected, and was readily recognised as ethylic acetate by its characteristic odour. The yield was about 9 grams.

*Benzoic Acid.*—Twenty grams of benzoic acid covered with pure dry ether were saturated with gaseous hydrogen bromide and allowed to stand for a few days. It was then heated for some time on a water bath to free it from hydrogen bromide, shaken with excess of sodium carbonate solution to remove any free benzoic acid, extracted with ether, dried over calcium chloride, and distilled. The portions distilling between  $209^{\circ}$  and  $212^{\circ}$  weighed 11 grams.

*Stearic Acid.*—Some stearic acid was treated in exactly the same manner with ether and hydrogen bromide, and after a few days shaken up with a dilute sodium carbonate solution, the ether evaporated, and the waxy-looking residue crystallised from alcohol. The crystals, dried and freed from alcohol in a vacuum desiccator, were recognised as ethylic stearate by their appearance and melting point ( $33^{\circ}$ ).

*Boric Acid.*—Crystallised boric acid was covered with ether, saturated with hydrogen bromide, and after being allowed to stand for two days was distilled under reduced pressure to remove free hydrogen bromide and ether. The portions collected between  $115^{\circ}$  and  $120^{\circ}$  were redistilled under atmospheric pressure.

The product burnt with a green flame, and was quickly decomposed



by water, giving boric acid and ethylic alcohol. The quantity obtained, however, was but small.

The yields appear to be fairly good in most instances, and the process may, in certain special cases, have a practical advantage over the usual methods of preparing ethylic salts; the principal object of this part of the investigation, however, was to demonstrate that the change is a general one, that is to say, that the acid interacts with ether in presence of dry hydrogen bromide to form an ethylic salt.

Experiments were then made with a view of ascertaining the behaviour of organic compounds other than acids when submitted to a similar treatment; the first group of substances selected was that of the carbohydrates and some of the allied alcohols.

*Cane-sugar*.—The powdered substance was covered with anhydrous ether, and dry hydrogen bromide was passed into the mixture nearly to saturation, the vessel being surrounded by cold water. At first, only a yellow coloration was produced, but after the mixture had been allowed to stand for about an hour at the ordinary temperature, a beautiful and intense *purple colour* was developed, both in the solution and in the undissolved solid, and remained permanent for some days.

On adding water, the colour is immediately discharged, and a greenish-black precipitate separates which dissolves in concentrated sulphuric acid with a purple colour.

On evaporating the purple ethereal solution in a vacuum over sulphuric acid and solid potash, a purplish-black, gummy mass remains, and a similar effect is produced by precipitation with light petroleum. If the purple solution is treated with excess of anhydrous sodium carbonate, a yellow mass is obtained from which ether extracts a substance that gives the purple coloration with concentrated sulphuric acid. It is left as a yellow gum on evaporating the ether, but on adding light petroleum it is partially precipitated in yellow flocks which dry up in a vacuum to a buff-yellow powder. This again gives the purple colour with sulphuric acid.

The properties of this substance seem closely to resemble those of the compound which has been described by Stenhouse and others as 'metafurfurol,' which is obtained in small quantity in the ordinary preparation of furfuraldehyde. It does not appear, however, to be volatile, as it could not be detected in the distillate when either the acid or alkaline mixtures, above referred to, were distilled under reduced pressure or in a current of steam. The nature of this substance is still under investigation.

A similar colour reaction cannot be obtained by substituting *hydrogen chloride* for *hydrogen bromide*, only a slight reddish coloration being obtained even after long standing; and hydrogen iodide merely gives



a separation of iodine. Subsequent experiments have shown, however, that the *ether* is not essential. If powdered cane-sugar be shaken in a stoppered bottle filled with dry hydrogen bromide, the gas is slowly absorbed, and the solid becomes first pink and then deep purple. The colour, however, is not so permanent as when ether is employed, being changed to black after some hours.

In order to compare the behaviour of other carbohydrates, &c., with that of cane-sugar under uniform conditions, about 0.5 gram of the powdered substance was placed in a stoppered bottle and covered with 7.5 c.c. of anhydrous ether which had previously been saturated with dry hydrogen bromide at about 15°. With these proportions, cane-sugar gives an intense purple colour in about an hour and a half.

*Milk-sugar, maltose, dextrose, galactose, xylose*, and the *synthetical sugar* obtained by condensation of glycollic aldehyde (Trans., 1897, 71, 377) give only varying shades of yellow, brown, or red, even after standing for several hours, but after the mixtures have remained for periods of about 24 hours a certain amount of *purple* colour is obtained in each case. The intensity and brilliancy of this colour, however, even after standing for several days, never even distantly approaches that obtained with cane-sugar after it has stood for about an hour and a half. The colour obtained with xylose is more intense than that given with the other substances mentioned in this group, and appears rather more quickly.

*Lævulose* (crystallised), on the other hand, when treated in a similar way, gives a much more energetic reaction than cane-sugar, a red colour being developed after a minute or two, and becoming intensely purple after about half an hour. The dry substance absorbs hydrogen bromide, almost instantaneously becoming deep purple. The absorption of the gas is extremely rapid, and forms a striking experiment when the powdered substance is placed in a jar of hydrogen bromide over mercury; a small jar is completely filled in about 5—10 minutes, whilst in the case of cane-sugar a similar absorption takes about 5 hours.

Dry hydrogen chloride also gives a certain amount of purple colour with lævulose, which is soon changed to black; and an ethereal solution of hydrogen chloride gives a red colour after the lapse of some hours.

*Glycollic aldehyde* (Trans., 1895, 67, 774) and *arabinose* give only various shades of orange and brownish-red, without any trace of purple, even on long standing.

*Starch, glycogen, cellulose, gum, mannitol, dulcitol, sorbitol, erythritol*, and *glycerol* all produce merely a yellow colour.

*Dextrin* gives no colour until after the mixture has stood for about 24 hours, when a very faint trace of purple colour becomes apparent.

*Inulin*, however, after standing for about 1—2 hours, gives an *intense purple colour* resembling that from cane-sugar or lævulose.

*Sorbose* behaves exactly like *lævulose*, giving an intense purple colour after about half an hour.

*Rhamnose* behaves in the first instance like *arabinose*, giving only an orange or red colour after about 24 hours; but on longer standing a certain amount of purple colour is obtained.

Mucic, saccharic and manno-saccharic acids give no colour.

The carbohydrates which have so far been examined may conveniently be classified with regard to their behaviour towards hydrogen bromide in ethereal solution in the following manner.

*a.* Those which give an *intense* purple coloration after standing for *two hours* or less.

*b.* Those which give a purple colour of relatively moderate intensity only after standing for *a day* or *two*.

*c.* Those which give a deep red or brown colour without any tinge of purple, even on long standing, and

*d.* Those which remain unaffected, or give only a yellow colour.

On reference to the examples given, it will be observed that the substances which behave as in *a* are either *ketoheoses* or are carbohydrates capable of producing these on hydrolysis.

Substances which behave as in *b* are *hexaldoses* or carbohydrates which give rise to them, whilst glycollic aldehyde (dialdose) and *arabinose* (pentaldose), behave according to *c*. The behaviour of *rhamnose* (methylpentose) appears to be intermediate between *b* and *c*. *Xylose* (pentaldose), however, shows a behaviour similar to the *hexaldoses*; with this exception, it would appear that the production of any purple colour, either quickly or slowly, is indicative of *ketoheoses*, *hexaldoses*, or substances which give rise to these. It is of course possible that this exception is due to impurity in the *xylose* employed. It was, however, the purest obtainable specimen, recrystallised.

This colour reaction may be of service as a general method of distinguishing certain types of carbohydrates, especially those which behave as in *a*, the reaction for which is very characteristic; and it may, perhaps, be employed for showing the presence of such carbohydrates in natural products, &c.

*Cork* and *bran* become purple-violet after the mixture has remained for a few hours, whilst unripe fruits (*gooseberries* and *currants*, for example) give the coloration after a few minutes.

NOTE.—Professor Tilden has called our attention to the fact that *terpineol*, and also many essential oils, give a purple coloration when treated with gaseous hydrogen chloride (*Trans.*, 1879, 35, 286), and we find that a somewhat similar effect is produced by a solution of hydrogen bromide in ether. This colour does not, however, appear to have

any connection with that which is obtained with carbohydrates, and the effects are easily distinguished. In the case of terpineol, the maximum colour-intensity, which is relatively very slight, is obtained immediately and fades on adding more of the reagent.

## LVIII.—*Researches on Camphoric Acid.*

By SAMUEL BARNETT SCHRYVER.

"IN experimenting on the constitution of camphoric acid, one of the most characteristic properties which at once presents itself is the great stability of the acid, which makes it very difficult to attack it by reagents and thus resolve it into smaller molecules."

With these words, Prof. W. H. Perkin and Dr. Crossley preface their paper, which opens the current volume of the transactions of this Society. They may equally well stand at the head of the present communication. It seems desirable, however, not only that camphoric acid should be resolved into smaller molecules, but also that the reactions by which this purpose is accomplished should take place at comparatively low temperatures. With this purpose in view, the following work was undertaken.

Sodium ethoxide acts in various ways on the ethylic salts of monobasic lactone acids, to which class camphanic acid (oxycamphoric acid) belongs; terebic acid, for example, is converted by this means into the unsaturated teraconic acid (Roser, *Annalen*, 1883, 220, 255). It was found that no action took place when ethylic camphanate was treated either by sodium ethoxide in alcoholic solution, or by sodium in ethereal solution, under varying conditions.

### *Lauronolic Acid.*

Having failed to prepare from camphoric acid an unsaturated acid in the way described above, attention was next turned to lauronolic acid, which was originally prepared by Woringer (*Annalen*, 1885, 227, 7) by the destructive distillation of camphanic acid. More recently, however, Aschan (*Ber.*, 1894, 27, 3507) showed that it could be prepared directly from bromocamphoric anhydride by treating it with sodium carbonate, thereby proving that the bromine atom is in the  $\alpha$ -position. Previously, however, to the publication of Aschan's paper, the author of the present communication had commenced the investigation of lauronolic acid, more especially of the oxidation products of this substance, and on informing Dr. Aschan of this, he courteously abandoned this field; the author takes this opportunity of expressing

his obligations to Dr. Aschan, and of acknowledging the very great assistance he has received in carrying out the following difficult and tedious work by the publication above referred to.

*Preparation of Bromocamphoric Anhydride and Lauronolic Acid.*

The method adopted for preparing these substances was essentially that of Aschan, namely, converting camphoric acid first into its chloride by means of phosphorus pentachloride, and brominating the product thus formed in presence of the phosphorus compounds. Usually, 250 grams of acid were brominated at a time, 50 grams of acid and 105 grams of pentachloride being introduced alternately into the flask, as it is not advisable to mix the whole of the 250 grams and the corresponding amount of chloride at once. After brominating, the contents were thrown into a large quantity of water, the mixture being cooled as soon as the reaction begins to get violent; the lauronolic acid was then prepared from the product obtained, exactly according to Aschan's directions. Altogether about 160 grams of lauronolic acid are obtainable from 1 kilogram of camphoric acid.

*Oxidation of Lauronolic Acid by Potassium Permanganate.*

Ten grams of lauronolic acid were dissolved in dilute sodium carbonate solution, and ice cold 3 per cent. solution of potassium permanganate added drop by drop, shaking constantly; after the quantity corresponding with 4 atoms of available oxygen per molecule of acid has been added, oxidation with unsaturated acids generally proceeds very slowly, but this is not the case with lauronolic acid, as much more permanganate solution was added without any apparent retardation of the oxidation. The products of oxidation, which were isolated in the usual way, consisted of some unchanged lauronolic acid, small quantities of volatile fatty acids, oxalic acid, and another acid giving an insoluble lead salt, obtained after the oxalic acid had been separated as calcium oxalate, but in quantity far too small for further investigation. No other definite product was obtained. *In this respect, lauronolic acid behaves like the tetrahydrophthalic acids investigated by von Bayer, and differs from the majority of ordinary unsaturated acids.*

For this reason, and owing to the ease with which a nitro-derivative was formed (see below), it was thought that camphoric and lauronolic acids were hydrogenised benzene derivatives, and an attempt to synthesise camphoric acid on this assumption was made (Trans., 1898, 73, 68).



*Action of Nitric Acid on Lauronolic Acid.*

On treating lauronolic acid with nitric acid, a violent oxidation took place; the solid neutral product which separated was collected, and the filtrate neutralised with caustic soda and evaporated down to a small bulk; on adding silver nitrate, a copious, white precipitate was formed, which, after being washed with water, alcohol, and ether, was suspended in ether and decomposed by hydrogen sulphide; after filtering from the silver sulphide, and evaporating the ether, a solid acid was left which proved to be oxalic acid.

*Nitrocampholactone.\**

The solid substance mentioned in the preceding paragraph as obtained on treating lauronolic acid with nitric acid proved on investigation to be nitrocampholactone,  $C_9H_{13}O_2 \cdot NO_2$ . To obtain the best yield of this compound, the following method was employed; lauronolic acid in quantities of 5 grams at a time is dissolved in four or five times its volume of concentrated nitric acid of sp. gr. 1.45, and very gently warmed over a small flame in a reflux apparatus; as soon as action commences, the flask containing the mixture is immersed in cold water. When the violent reaction which takes place, accompanied by large quantities of nitrous fumes, abates, the mixture is cooled and poured into several times its volume of cold water. The oil which separates very quickly solidifies to a yellow, flocculent mass; this is collected, washed with cold water, and, after being dried on a porous plate, is recrystallised from absolute alcohol, from which it separates in nearly white, skeleton, quadratic prisms melting at  $170^\circ$ . This product is generally pure enough for all further operations. Another crop of crystals can generally be obtained by adding a little water to the mother liquor, but if too much water is added an oil separates. The crystals are almost insoluble in water and dilute alkalis, neutral to litmus paper, and readily soluble in alcohol, ether, light petroleum, and most other organic solvents. For analysis, they were twice crystallised from absolute alcohol, and finally from light petroleum, separating from the latter in the form of scalenohedric quadruplets melting at  $171^\circ$ . They volatilise even below  $100^\circ$ .†

\* Campholactone is isomeric with lauronolic acid and obtained from it very readily by treatment with acids.

† A small quantity of this substance (a fraction of a gram) was obtained by Reyher (*Dissert.*, Leipzig, 1891), but he did not recognise its nature. One of the analyses quoted is taken from his paper.



0.2062 gave 0.4140  $\text{CO}_2$  and 0.1234  $\text{H}_2\text{O}$ .

0.2045 „ 0.4111  $\text{CO}_2$  „ 0.1232  $\text{H}_2\text{O}$ .

0.3618 „ 21.8 c.c. moist nitrogen at  $9^\circ$  and 757 mm.

0.1944 „ 13.0 c.c. „ „  $19^\circ$  and 739 mm.

Found.  $\text{C} = 54.75$  and  $54.79$ ;  $\text{H} = 6.65$  and  $6.69$ ;  $\text{N} = 7.05$  and  $7.44$ .  $\text{C}_9\text{H}_{13}\text{O}_2\cdot\text{NO}_2$  requires  $\text{C} = 54.29$ ;  $\text{H} = 6.53$ ;  $\text{N} = 7.04$  per cent.

Careful experiments were made to obtain an oxime derivative but with a negative result, so that the compound is not a ketone.

Attempts were made to produce this nitro-derivative without warming; lauronolic acid is, however, not acted on in the cold even by fuming nitric acid, when in acetic acid solution, and consequently, owing to oxidation, the yield of nitrocampholactone is not large. Generally, the amount of crude nitro-compound only amounts to about one-third of the weight of the lauronolic acid used. Nitrocampholactone can, however, be best prepared by the action of nitrogen peroxide on lauronolic acid.

#### *Action of Nitrogen Peroxide on Lauronolic Acid.*

Béhal and Blaise (*Compt. rend.*, 1895, 121, 238) have shown that campholenic acid absorbs nitrogen peroxide, forming a somewhat unstable blue compound which they called “cerulæonitrosodihydrocampholenoactone,” and this, by the further action of nitrogen peroxide, yields the colourless nitro-derivative. Tiemann subsequently (*Ber.*, 1897, 30, 412) prepared the same compound by the action of nitric acid on campholenic acid. All three observers are agreed as to the nature of this substance, and of the error of Kächler and Spitzer, who obtained it previously and called it nitrocampholenic acid.

Lauronolic acid appears to behave in every way like campholenic acid; in fact, nitrocampholactone can be more conveniently prepared by the action of nitrogen peroxide on lauronolic acid than by the action of nitric acid. A few grams of lauronolic acid in a shallow layer in a flat-bottomed evaporating basin are exposed to the fumes of nitric peroxide, obtained by heating lead nitrate, and passed over the acid by means of an inverted funnel; the fumes are rapidly absorbed and the liquid becomes dark greenish-blue. After a time, oxidation takes place, the liquid becomes warm and rapidly loses its colour, and on cooling solidifies to an indistinct, crystalline mass, which, however, still has a greenish tint. The solid, after being exposed to the air for some time, and finally dried in a vacuum over quicklime to get rid of the excess of acid, is spread on a porous plate and the dried mass recrystallised

from absolute alcohol. The nitrolactone thus prepared is identical with the product obtained by the action of nitric acid.

The nitroso-derivative prepared in the above way was not directly isolated ; a better method is described in detail below.

*Action of Nitric Acid on Campholactone.*

When campholactone is treated with concentrated nitric acid, no action takes place in the cold, but on warming, a violent oxidation takes place, and on cooling, a certain quantity of nitrocampholactone separates. The yield obtained, however, is considerably smaller than that obtained by the action of nitric acid on lauronic acid.

*Reduction of the Nitrolactone by Zinc Dust and Glacial Acetic Acid.  
Hydroxylaminolactone.*

Nitrocampholactone, dissolved in about ten times its weight of glacial acetic acid, is cooled by ice cold water, and zinc dust added in small quantities at a time ; as soon as the further addition of zinc dust causes no very appreciable rise in temperature, the action is complete. The solution is filtered from the excess of zinc dust and zinc acetate, the residue washed with as small a quantity of water as possible, and the filtrate and washings made strongly alkaline by concentrated solution of caustic soda, the temperature being kept low meanwhile by cooling with ice ; the turbid liquid is then extracted about six times with ether. On distilling off the ether, a syrup is left, which very rapidly solidifies to a crystalline mass of bluish-green tinge ; as the product is readily soluble in hot water, it can easily be separated from the small quantity of nitrosolactone which is formed at the same time, and is described in greater detail below. From the hot aqueous solution thus obtained, the substance separates in characteristic, twinned, quadratic prisms ; these are but slightly soluble in light petroleum, but readily in ether, and can be conveniently recrystallised by dissolving in the latter and precipitating by the addition of light petroleum. When finally recrystallised from absolute ether, they melt sharply at  $148^{\circ}$ .

0.2075 gave 0.4468  $\text{CO}_2$  and 0.1570  $\text{H}_2\text{O}$ .  $\text{C} = 58.38$  ;  $\text{H} = 8.11$ .

0.1976 „ 13.1 c.c. moist nitrogen at  $15^{\circ}$  and 730 mm.  $\text{N} = 7.51$ .

0.2038 „ 14.2 c.c. „ „ „  $19^{\circ}$  „ 740 mm.  $\text{N} = 7.82$ .

$\text{C}_9\text{H}_{13}\text{O}_2\cdot\text{NH}\cdot\text{OH}$  requires  $\text{C} = 58.47$  ;  $\text{H} = 8.40$  ;  $\text{N} = 7.45$  per cent.

This compound, from the results of the analysis, appears to be the *hydroxylamino*-derivative. It is not of very basic character, and does not give a precipitate when gaseous hydrogen chloride is passed into its ethereal solution. Furthermore, it reduces ammoniacal silver nitrate

*almost immediately in the cold* and also Fehling's solution, and is oxidised by ferric chloride.

This production of a hydroxylamine is noteworthy. Bamberger (*Ber.* 1894, 27, 1347 and 1548) shows that nitrobenzene is capable of being reduced by means of zinc dust in water, and Wohl (*ibid.*, 1432) obtained a similar result; Bamberger finds, however, that phenyl-hydroxylamine is very unstable in presence of acids and also when boiled with water. Gattermann (*Ber.*, 1893, 26, 1844 and 2810, also 1894, 27, 1927) shows that various aromatic nitro-derivatives, on reduction by electrolytic hydrogen, yield amidohydroxy-derivatives, the hydroxylamine derivatives apparently being produced in the first instance, and changing in the presence of acids into the isomeric amidohydroxy-compounds. The product obtained by the reduction of nitrocampholactone by the method described above was, however, obtained in acid solution, and is so stable in the presence of water that it can be recrystallised from it.

It appears, therefore, that, *whereas, on the one hand, lauronolic acid, like an aromatic derivative, on treatment with nitric acid yields a nitro-derivative with the greatest ease, this nitro-derivative, on reduction, yields a hydroxylamino-compound which is far more stable than a similar compound obtainable from a benzene derivative.*

*Action of Ferric Chloride on Hydroxylaminocampholactone  
Nitrosocampholactone.*

It has been mentioned above that hydroxylaminocampholactone reduces ferric chloride; by this means, a nitroso-derivative can be produced. On adding ferric chloride in excess to a solution of the hydroxylamino-compound in water, a light, bluish-green, flocculent precipitate is formed which is excessively soluble in ether, the precipitate being immediately dissolved on shaking with ether, yielding a dark bluish-green solution; on evaporating the ether, the nitroso-derivative remains behind as a bluish-green, indistinct, crystalline mass of pungent, camphor-like odour. It is excessively soluble in ether, light petroleum, ethylic and methylic alcohols, and most organic solvents, and for this reason it is extremely difficult to purify it. It can be prepared directly from the nitro-derivative without the isolation of the intermediate hydroxylamino-derivative; for this purpose, the nitro-derivative is reduced by means of glacial acetic acid and zinc dust in the manner above described and the zinc acetate and zinc dust filtered off; water is then added, and any unchanged nitro-derivative which may be precipitated is filtered off. To the filtrate, ferric chloride is directly added, the precipitated nitroso-compound extracted with ether, and the ether evaporated, when the nitroso-deriva-

tive remains behind in acetic acid solution; on adding water, the nitroso-derivative separates as an oil which, on standing in a desiccator, solidifies almost entirely. The bright green, crystalline plates thus obtained, when dried on a porous plate to separate them from a small amount of impurity, melt fairly sharply at  $117^{\circ}$ . The specimen used for analysis was recrystallised from methylic alcohol.

0.2096 gave 13.5 c.c. moist nitrogen at  $9^{\circ}$  and 748.3 mm.  $N = 7.71$ .

$C_9H_{13}O_2 \cdot NO$  requires  $N = 7.65$  per cent.

The substance analysed, although crystalline, was somewhat resinous to the touch, and probably the melting point given is not absolutely correct, owing to the difficulty of purifying comparatively small quantities. The nitroso-derivative, with phenol and concentrated sulphuric acid, gave a dark green solution, becoming pink on diluting with water and giving a transient green coloration on the addition of caustic potash (Liebermann's reaction for nitroso-compounds). There is no doubt, therefore, as to the chemical nature of the compound.

*Reduction of Nitrocampholactone by Tin and Hydrochloric Acid.*  
*Aminocampholactone.*

The amino-derivative is obtained by reducing the nitro-derivative with tin and hydrochloric acid; for this purpose, it is suspended in strong hydrochloric acid and granulated tin added, when the solution becomes warm, and the solid nitro-derivative gradually disappears, giving rise to a dark green solution; on further action of the nascent hydrogen, the solution loses its colour, finally becoming light yellow. The nitroso-compound appears to be formed as an intermediate product; the course of the reaction, therefore, can be readily followed. When the reduction is complete, a concentrated solution of caustic soda is added to the cooled acid liquid until the mixture is strongly alkaline, and the turbid liquid is then extracted six or seven times with ether; on evaporating the ether, the aminolactone is left. If the pure nitro-compound had been used and the operation carefully carried out, the amino-derivative solidifies in a very short time to a mass of hard crystals, which, after a couple of recrystallisations from water, are quite pure. As a general rule, however, the amino-derivative is obtained as an oil which only partially solidifies, even after standing for some days in a vacuum; in this case, it is best purified by dissolving the dried substance in absolute ether, and precipitating as hydrochloride by dry hydrogen chloride. The salt then separates as a snow-white, crystalline mass which is very soluble in water; the yield of hydrochloride from the nitro-compound is a little more than 75 per cent. of the theoretical. To obtain the free base, the hydrochloride is dissolved in a small quantity of water, and the solution put into a separating funnel under ether; potassium carbonate is then



added drop by drop in strong solution, and the free base immediately extracted with ether after each addition of alkali. On evaporating the ether under diminished pressure, the base is left as a snow-white, crystalline mass readily soluble in ether and water, but only slightly in light petroleum. For analysis, it was twice recrystallised from hot water, from which it separates in large, pearly plates melting at  $39^{\circ}$ ; these plates, however, contain a considerable quantity of water, but on drying in a vacuum they effloresce and give up water, the dried crystals melting at  $66^{\circ}$ .

0.2014 gave 14.9 c.c. moist nitrogen at  $21^{\circ}$  and 740 mm.  $N = 8.35$ .

0.1370 „ 0.3230  $CO_2$  and 0.1130  $H_2O$ .  $C = 64.28$ ;  $H = 9.16$ .

$C_9H_{13}O_2 \cdot NH_2$  requires  $C = 63.90$ ;  $H = 8.88$ ;  $N = 8.28$  per cent.

The *hydrochloride* precipitated from its ethereal solution as above described is dissolved in water, and, if necessary, decolorised by boiling with animal charcoal; on filtering and evaporating, the hydrochloride separates in white, silky needles, which are dried on blotting-paper and then in vacuum, and finally purified by dissolving in absolute alcohol and slowly precipitating from the alcoholic solution by ether. They are thus obtained in small, white prisms which decompose without melting above  $200^{\circ}$ .

0.2312 gram requires 11.6 c.c.  $AgNO_3$  solution, of which 1 c.c. = 0.00348 gram  $Ag$ .  $Cl = 17.46$ .

$C_9H_{13}O_2 \cdot NH_2 \cdot HCl$  requires  $Cl = 17.76$  per cent.

*Platinochloride*.—On adding platinum tetrachloride in strong solution to a concentrated solution of the hydrochloride, the platinochloride separates in glistening, golden-yellow needles, *but only after standing for some time*, as it is very soluble in water. The crystals, after being drained, are dried on a porous plate, and finally purified by dissolving in absolute alcohol and precipitating from the alcoholic solution by ether. The salt is thus obtained in pale, golden-yellow spangles which decompose without melting above  $200^{\circ}$ . An analysis shows that they are the platinochloride, *not* of the aminolactone itself, but of the corresponding aminohydroxy-acid.

0.3421 gave 0.0850 Pt.  $Pt = 24.84$ .

0.6432 „ 0.1587 Pt.  $Pt = 24.67$ .

$(C_9H_{15}O_3 \cdot NH_2)_2, H_2PtCl_6$  requires  $Pt = 24.90$  per cent.

$(C_9H_{13}O_2 \cdot NH_2)_2, H_2PtCl_6$  „  $Pt = 26.1$  „

*Action of Potassium Nitrite on the Hydrochloride of the Amine.*

On treating a strong, ice cold solution of the hydrochloride of the amine with potassium nitrite, the nitrite of the base separates. This, however, is very unstable, and decomposes on warming gently with



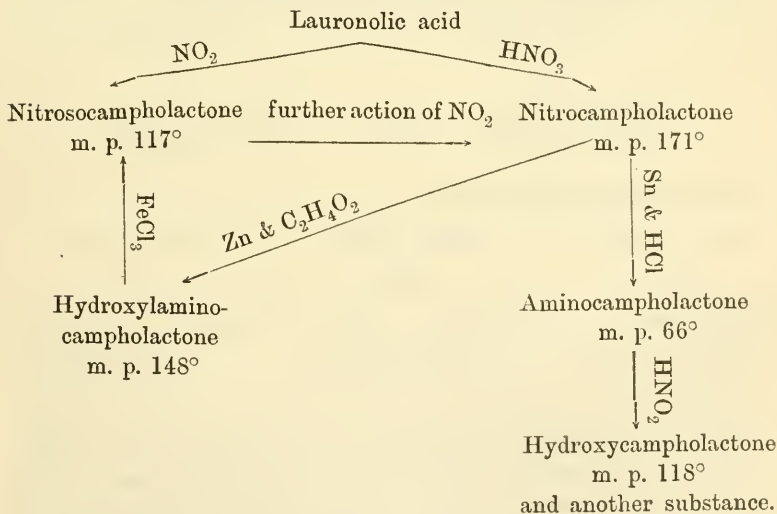
water giving two products; an oil separates, but on adding caustic soda a part of this dissolves, and on extracting the alkaline solution with ether a neutral oil is obtained with characteristic, sweet, peppermint-like odour. On acidifying the residual alkaline solution, and extracting again with ether, a substance is obtained which solidifies in part on standing; the solid crystals thus obtained, after being dried on a porous place, are readily soluble in ether, but not in light petroleum, and can, therefore, be purified by dissolving in the former solvent and precipitating the solution by the latter. They then melt at  $118^{\circ}$ .

The best conditions for carrying out this reaction have not yet been obtained.

These compounds must be reserved for future investigation. Tiemann (*Ber.*, 1897, 30, 414) has shown that aminodihydrocampholenolactone, by a similar reaction, yields hydroxydihydrocampholenolactone and a campholenolactone, whilst Angeli (*Ber.*, 1893, 26, 1718) obtained camphenone from aminocampholenolactone. Probably an analogous reaction here takes place, the elements of water being removed at the same time that the amino-group is replaced by the hydroxy-group.

### Conclusions.

The reactions described above may be schematically represented as follows.

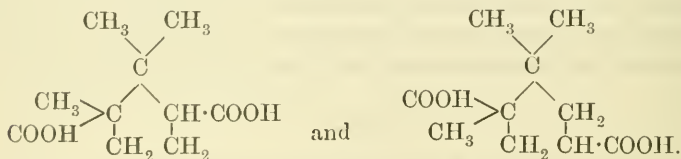


Piloty has recently (*Ber.*, 1898, 31, 219) been investigating aliphatic nitroso-derivatives, and he concludes from a large number of examples that true nitroso-derivatives are only obtained with ease from those

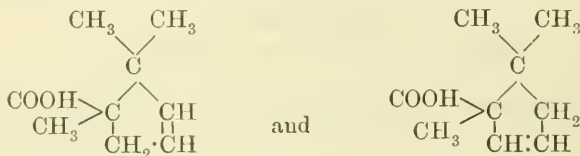
hydroxylamino-compounds in which the  $\text{-NH}\cdot\text{OH}$  group is attached to a tertiary carbon atom. This conclusion has such an important bearing on the above work that it seems worth while to give Piloty's own words. Speaking of the nitroso-derivatives, he writes.

"Alle diese Substanzen haben das gemeinsame Merkmal das sie die Stickoxylgruppe an Kohlenstoff gebunden erhalten der keinen Wasserstoff mehr besitzen. Wohl (*Ber.*, 1894, 27, 1435), und Bamberger (*ibid.*, 1537) fanden gleichzeitig das Phenylhydroxylamin durch Oxydationsmittel in Nitrosobenzol verwandelt werden kann. . . . Aus der Gesammtheit dieser Thatsachen muss der Schluss gezogen werden dass eine ausgesprochene Neigung zur Bildung wahrer Nitrosoverbindungen nur den Körpern eigen ist welche den Stickstoff an ein in Uebrigen tertiär gebundenes Kohlenstoffatom gekuppelt erhalten."

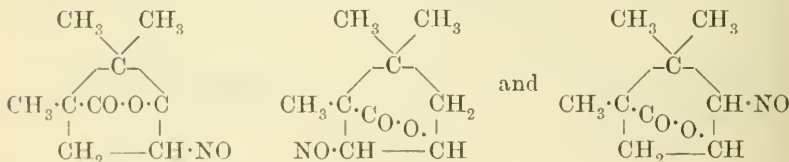
Now the formulæ for camphoric acid most in accordance with the known constitution of camphoronic acid are those of Brecht and W. H. Perkin, junr., namely,



These can give rise to the following lauronic acids,



and the following nitrosolactones,



The nitroso-group must in each case be attached to the carbon next to the lactone hydroxyl group, owing to the formation of the nitrosolactone by direct addition of  $\text{NO}_2$  to the unsaturated lauronic acid.

In none of the above cases is the nitroso-group attached to a tertiary carbon atom. Hence, if Piloty's generalisation is universally applicable, neither the Brecht nor the Perkin formula can represent the true constitution of camphoric acid.

Apart from this question, it can readily be seen from the above formulæ that, by replacing the nitro-group by the hydroxy-group, we can obtain a product capable of undergoing various reactions at comparatively low temperatures which might throw much light on the constitution of camphoric acid. The investigation of the product thus obtained would, however, entail the use of very large quantities of camphoric acid, and could hardly be undertaken single-handed under the conditions of ordinary laboratory work.

The greater part of the above work was carried out at University College, Liverpool, during my tenure of a demonstratorship of that Institution, and it was completed at the Royal College of Science, London. The expenses were partly defrayed by two grants (in 1894 and 1895) from the Government funds at the disposal of the Royal Society, and to the Committees charged with the distribution my best thanks are due.

#### *Addendum.*

In the Proceedings, 1898, page 111, there is a communication from Messrs. R. W. Collinson and W. H. Perkin on lauronolic acid, in which they state that, on oxidising the latter, an acid of the formula  $C_9H_{14}O_5$  is formed. Although this result is apparently not in harmony with those I have obtained, the contradiction seems to me to be more apparent than real, for it is known that unsaturated acids can be oxidised in stages by treatment with permanganate solution, and the acid they obtained is doubtless an intermediate product of oxidation.

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### LIX.—*Studies of the Terpenes and Allied Compounds.* *Stereoisomeric Derivatives of Camphor.*

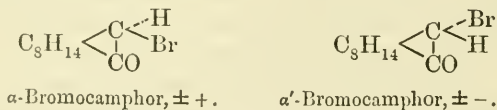
By T. MARTIN LOWRY, B.Sc.

WHATEVER the ultimate structure of the camphor molecule may be, there can be no doubt as to the presence in it of the group  $-CH_2 \cdot CO-$ , and the constitutional formula may therefore be written in an abbreviated form as  $C_8H_{14} \begin{smallmatrix} < CH_2 \\ | \\ CO \end{smallmatrix}$ . When one of the hydrogen atoms

of this group is displaced by another radicle, the carbon atom to which this is attached becomes asymmetric: consequently, two forms of mono-substitution derivatives may be produced by displacing one or other of the hydrogen atoms; and as the camphor molecule is itself optically active and therefore asymmetric, these two forms will not be mere

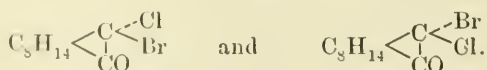
optical isomerides, differing only in the sense in which they rotate the plane of polarisation, but will be stereoisomerides differing also from one another in their other physical properties.

If the conclusion arrived at by Aschan be accepted, that camphoric acid contains two asymmetric carbon atoms, it is probable that the camphor molecule also contains two such atoms. Dextrcamphor will correspond to a *cis*-camphoric acid, and may be represented by the symbol  $\pm$ . We may then represent the two products obtained by displacement of the two hydrogen atoms of the  $-\text{CH}_2\cdot\text{CO}-$  group by the symbols  $\pm +$  and  $\pm -$ . In order to distinguish between the positions occupied by the two hydrogen atoms of the  $-\text{CH}_2\cdot\text{CO}-$  group, we may represent the position occupied by the bromine atom of ordinary monobromocamphor as the " $\alpha$ "-position, and in order to recall the increased dextrorotation produced by the displacement of this hydrogen atom, we may choose the symbol  $\pm +$  for all  $\alpha$ -substitution products. The stereoisomeride produced by the displacement of the other hydrogen atom will then be represented by the symbol  $\pm -$ , and the position occupied by the substituting radicle may be distinguished as the " $\alpha'$ "-position. The two forms may be represented by structural formulæ, thus.



In addition to the two " $\alpha$ "-positions, there appear to be only two other positions in the camphor molecule in which substitution takes place. One of these is the position occupied by the second bromine atom in  $\beta\alpha$ -dibromocamphor melting at  $113^\circ$ , and will be referred to throughout this paper as the " $\beta$ "-position; its location in the molecule is not definitely known, but the readiness with which the halogen is displaced seems to point to a tertiary position, such as is shown in Bredt's formula adjacent to the  $-\text{CH}_2\cdot\text{CO}-$  group. The other position is that in which sulphonation takes place under the influence of sulphuric anhydride, and is known as the  $\pi$ -position.

Stereoisomerism occurs, not only in the case of the mono-derivatives, but also in the case of the di-derivatives if the two hydrogen atoms of the  $-\text{CH}_2\cdot\text{CO}-$  group are displaced by different radicles. Thus two forms—an  $aa'$  and an  $a'a$ —are possible of chlorobromocamphor, as represented by the formulæ



As the conditions satisfied in the case of stereoisomeric camphor

derivatives also involve the introduction of a third asymmetric carbon atom into the molecule, it may be anticipated that, in most cases, a marked change in rotatory power will occur, and that this is so may be seen from a number of examples, thus :

Camphor .....	$[\alpha]_D = +42^\circ$ (in spirit).
$\alpha$ -bromocamphor .....	$[\alpha]_D = +135^\circ$ (spirit).
$\alpha$ -chlorocamphor .....	$[\alpha]_D = +96^\circ$ (spirit).
$\alpha$ -chlor- $\alpha'$ -bromocamphor.....	$[\alpha]_D = +10^\circ$ (chloroform).
$\alpha'$ -nitrocamphor .....	$[\alpha]_D = -124^\circ$ (benzene).

But when substitution does not produce stereoisomerism, and consequently no new asymmetric carbon atom is introduced, the change in specific rotatory power is much smaller, thus :

Camphor .....	$[\alpha]_D = +42^\circ$ (spirit).
$\alpha\alpha'$ -dibromocamphor .....	$[\alpha]_D = +39\cdot2^\circ$ (benzene).
$\alpha\alpha'$ -dichlorocamphor .....	$[\alpha]_D = +57\cdot3^\circ$ (spirit).

Further, it is to be anticipated that the two stereoisomerides, represented by the symbols  $\pm +$  and  $\pm -$ , will have specific rotatory powers differing in opposite senses, although not necessarily to the same extent, from that of allied compounds in which the  $\alpha$ -carbon atom is not asymmetric. Thus, on account of the high dextrorotatory power of  $\alpha$ -bromocamphor and  $\alpha$ -chlorocamphor, we may expect that the rotatory power of  $\alpha'$ -bromocamphor and  $\alpha'$ -chlorocamphor will be considerably lower than that of camphor. An example is found in the case of the bromochlorocamphors described in this paper, where we have

$\alpha$ -chlor- $\alpha'$ -bromocamphor .....	$[\alpha]_D = 10^\circ$
$\alpha$ -brom- $\alpha'$ -chlorocamphor .....	$[\alpha]_D > 64^\circ$ ,

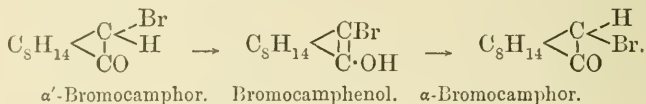
whilst camphor, dibromocamphor, and dichlorocamphor show an intermediate rotatory power.

The similarity or dissimilarity of two stereoisomerides will depend on that of the radicles occupying the  $\alpha$ - and  $\alpha'$ -positions. Thus the difference will be much more marked where these are H and Br, or H and  $\text{NO}_2$ , or Br and  $\text{NO}_2$ , than when both are halogens, and it has already been pointed out that when both radicles are identical the isomerism disappears. In the cases described in this paper, where the isomerism is produced by the interchange of chlorine and bromine atoms, it has been found that the isomerides are extremely similar, and crystallise together as isomorphous mixtures which behave in many respects as single substances.

The stability of the two isomeric forms varies in a very marked way, according as one or both of the  $\alpha$ -hydrogen atoms are displaced, the latter class of compounds being far more stable than the former.

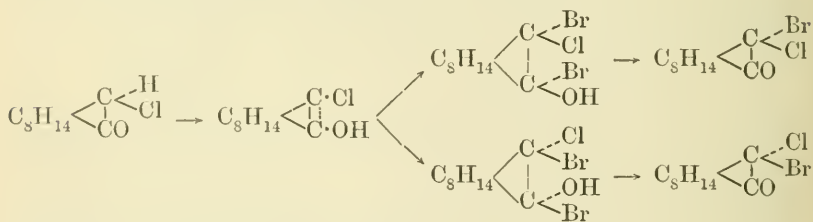


Beckmann has suggested (*Annalen*, 1889, 250, 365) that, in the case of the menthones, the stereoisomeric change is brought about by means of an intermediate 'enolic' form, and this suggestion has been applied by Marsh (*Trans.*, 1890, 57, 832) to explain the instability of the second form of monobromocamphor. The change may be represented thus,



When both of the hydrogen atoms are displaced, an enolic form is no longer possible, so that the observed stability of the di-derivatives is in accordance with this theory.

In all cases in which a halogen displaces one of the  $\alpha$ -hydrogen atoms, it is probable that both stereoisomerides are initially produced, and that when only one isomeride is obtained the non-appearance of a second is to be explained by its instability under the conditions of experiment. The production of stereoisomeric di-derivatives is most readily explained by supposing that the action of the halogen involves addition to the enolic form of the mono-derivative: its two different products would then be formed according as the double bond were broken on one side or on the other, and on subsequent removal of hydrogen bromide two forms of the di-derivative would be generated. The action of bromine on chlorocamphor, where both stereoisomerides are produced, may be represented by formulæ thus:



The production of two stereoisomerides when chlorine or bromine acts on mono-derivatives of camphor affords evidence that the halogen does not act by directly displacing hydrogen, but in some such way as that already indicated; it is also probable that in the majority of its interactions camphor enters first into combination, in its enolic form, with the agent, and that the elements of water, hydrogen chloride, &c., are subsequently eliminated from the additive compound thus produced.

The number of cases in which stereoisomeric derivatives of camphor have been obtained is very small, and in almost every instance the substances have been exceedingly badly characterised. The  $\alpha$ -chloro-camphor which Cazeneuve obtained by passing chlorine into an alcoholic

solution of camphor (*Bull. Soc. Chim.*, [ii], 1882, 38, 9, and 1883, 39, 501) is a well crystallised compound melting sharply and constantly at  $93^{\circ}$ ,  $[\alpha]_D = 96^{\circ}$  (spirit), but the substance which he separated from the mother liquors of the  $\alpha$ -compound is described as separating from its solution in arborescent forms (m. p.  $95-100^{\circ}$ ,  $[\alpha]_D = 57^{\circ}$ ), and no attempt appears to have been made to obtain it in definite crystals of constant melting point and specific rotatory power. Although it is possible that this product contained  $\alpha'$ -chlorocamphor, as Cazeneuve supposed, yet the production of  $\alpha$ -chlorocamphor by the action of alcoholic potash and the low specific rotatory power can both be explained by the presence of camphor and dichlorocamphor as impurities. Apart from probabilities, therefore, the actual evidence for the existence of an  $\alpha'$ -chlorocamphor is exceedingly slight.

By brominating camphor in a similar way, Marsh (*Trans.*, 1890, 57, 828; 1891, 59, 968) obtained a mixture from which he was able to separate, in addition to ordinary  $\alpha$ -bromocamphor (m. p.  $76^{\circ}$  [ $\alpha$ ] $_D = 135^{\circ}$ ), a fraction of lower specific rotatory power; as the lowest value obtained ( $[\alpha]_D = 29.4^{\circ}$ ) was considerably lower than is given either by camphor or by dibromocamphor, it is evident that this fraction may have consisted largely of an  $\alpha'$ -bromocamphor. But the description of the product as "yellowish, soft and of a camphorous consistency" appears to indicate that other substances were present as impurities.

The bromocamphor and chlorocamphor which are said to be produced by the action of hypobromous and hypochlorous acids on camphor appear to be position isomerides of the ordinary forms and not stereoisomerides.

An isomeric nitrochlorocamphor has been described by Cazeneuve (*Bull. Soc. Chim.*, [ii], 1888, 49, 428), and by Schiff and Puliti (*Ber.*, 1883, 16, 888), and stereoisomerism has also been suggested in explanation of the isomerism of the various nitrocamphors and of nitrocamphor with camphornitrophenol (Lapworth and Kipping, *Trans.*, 1896, 69, 306). The question of stereoisomeric nitro-, bromonitro-, and chloronitro-camphors will be discussed in a subsequent paper on nitrocamphor, but I may here say that in no case do the experiments that I have made on these substances support the conclusion that we are dealing with stereoisomerides.

Two indubitable cases of stereoisomerism are considered in this paper. In each of the cases described, the two hydrogen atoms of the  $-\text{CH}_2\cdot\text{CO}-$  group are displaced by chlorine and bromine respectively, the two isomerides only differing in that the positions of the chlorine and bromine atoms are interchanged. They are, therefore, isomorphous as well as isomeric, and crystallise together in magnificent crystals which are very easily obtained free from impurity. The two forms can be approximately separated by a long series of crystal-

lisations, by means of which two fractions are obtained differing widely in rotatory power, but not greatly in other respects. In this way, the *aa*-bromochlorocamphor obtained by the direct action of bromine on chlorocamphor (Cazenueve, *Bull. Soc. Chim.*, 44, 118) has been separated into fractions of specific rotatory power  $[\alpha]_D = 64^\circ$  and  $[\alpha]_D = 16^\circ$ , that of the initial product being  $[\alpha]_D = 51^\circ$ . A mixture of the same two constituents in different proportions has been obtained by chlorinating bromocamphor; the initial rotatory power of this was  $[\alpha]_D = 26^\circ$  and it was separated into fractions giving the values  $[\alpha]_D = 28^\circ$  and  $[\alpha]_D = 10^\circ$ . By the action of bromine on chlorocamphor in sealed tubes, a dibromochlorocamphor has been obtained from which the less soluble stereoisomeride has been isolated in a pure state with a constant specific rotatory power  $[\alpha]_D = 51^\circ$ , that of the initial product being  $[\alpha]_D = 44^\circ$ . It is also shown in this paper that *aa*-dibromocamphor,  $\beta a$ -dibromocamphor, and  $\beta a$ -bromochlorocamphor are single substances and not mixtures of stereoisomerides.

The constitution of *a*-bromocamphor and *a*-chlorocamphor is proved by their oxidation to camphoric acid,



The products obtained by the further action of chlorine and bromine on these vary greatly according to the conditions. They may be divided into three groups, the members of each group forming an isomorphous series of crystals, and showing similar physical and chemical properties, as is seen in the following table.

	M. P.	$[\alpha]_D$	Axial Ratios.
I. The <i>aa</i> -series.			
<i>aa</i> -Dibromocamphor .....	60°	40°	1·5778 : 1·2·0685
<i>aa</i> -Bromochlorocamphor .....	55°	51°	1·5395 : 1·1·9144
<i>aa</i> -Chlorobromocamphor .....	58°	26°	1·5338 : 1·1·9020
<i>aa</i> -Dichlorocamphor .....	96°	57°	1·4820 : 1·1·8358
II. The $\beta a$ -series.			
$\beta a$ -Dibromocamphor .....	113°	100°	1·83 : 1·1·92
$\beta a$ -Bromochlorocamphor .....	98°	70°	
III. The $\beta aa$ -series.			
$\beta aa$ -Dibromochlorocamphor .....	81°	44°	1·4627 : 1·2·1332
$\beta aa$ -Tribromocamphor .....	64°		
$\beta aa$ -(?)-Trichlorocamphor .....	54°		

The members of the *aa*-series are for the most part prepared by the direct action of chlorine or bromine, whilst those of the  $\beta a$ - and

$\beta\alpha\alpha$ -series can only be obtained by the action of bromine in sealed tubes.

The present investigation of the derivatives of camphor containing halogen was undertaken with the object of obtaining data which might throw light on the constitution of these substances, and more especially on the nature of the isomeric change which occurs when the bromination of bromocamphor and chlorocamphor is carried out in sealed tubes. It will be well, therefore, at this point, to state what data are available for forming an opinion as to the constitution of these substances.

The nitrobromocamphor produced by the action of nitric acid on  $\alpha$ -bromocamphor undoubtedly has the constitution represented by the

formula  $C_8H_{14} \begin{smallmatrix} \diagup & C & \diagdown \\ & | & \\ & CO & \end{smallmatrix} \begin{smallmatrix} \diagup NO_2 \\ \diagdown Br \end{smallmatrix}$  as it is converted by reduction into  $\alpha'$ -nitro-

camphor,  $C_8H_{14} \begin{smallmatrix} \diagup & C & \diagdown \\ & | & \\ & CO & \end{smallmatrix} \begin{smallmatrix} \diagup NO_2 \\ \diagdown H \end{smallmatrix}$ , which is readily oxidised to camphoric acid,

and when decomposed by heat it yields camphorquinone,  $C_8H_{14} \begin{smallmatrix} \diagup & C & \diagdown \\ & | & \\ & CO & \end{smallmatrix} \begin{smallmatrix} \diagup CO \\ \diagdown CO \end{smallmatrix}$ ,

losing NOBr. It has been shown by Kachler and Spitzer (*Monatsh.*, 1882, 3, 218, and 1883, 4, 566) that, when heated with nitric acid,  $\beta\alpha$ -dibromocamphor, like  $\alpha$ -bromocamphor, yields a nitro-derivative, and that this, on reduction, yields an  $\alpha'$ -amidocamphor identical with that obtained by reducing  $\alpha'$ -nitrocamphor; it may, therefore, be represented by the

formula  $C_8H_{13}Br \begin{smallmatrix} \diagup & C & \diagdown \\ & | & \\ & CO & \end{smallmatrix} \begin{smallmatrix} \diagup H \\ \diagdown Br \end{smallmatrix}$ . The position in the molecule occupied

by the " $\beta$ "-bromine atom has not yet been definitely ascertained.  $\alpha\alpha$ -Dibromocamphor, however, does not yield a nitro-derivative, but undergoes oxidation (Kachler and Spitzer, *Monatsh.*, 1883, 4, 554; Forster, *Trans.*, 1896, 69, 36). The simplest explanation of the difference in the behaviour of the two isomerides is to be found in the presence in the  $\alpha\alpha$ -compound of a bromine atom in the position in which nitrations take place, so that its formula may be written

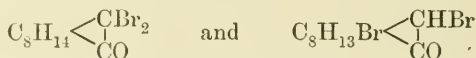
$C_8H_{14} \begin{smallmatrix} \diagup & CBr_2 \\ & | & \\ & CO & \end{smallmatrix}$ . An alternative formula has been suggested by Forster

(*loc. cit.*), who, in order to explain the formation of dibromocampholid and its derivatives, assumes the existence of the group  $\begin{smallmatrix} -CBr & CHBr \\ | & | \\ -C & -CO \end{smallmatrix}$ .

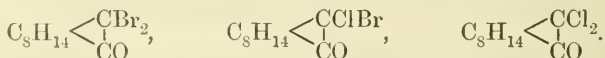
Without discussing the constitution of the camphor-molecule, we may write this formula as  $C_8H_{13}Br \begin{smallmatrix} \diagup & C & \diagdown \\ & | & \\ & CO & \end{smallmatrix} \begin{smallmatrix} \diagup Br \\ \diagdown H \end{smallmatrix}$  and regard it as the stereoisomeric form of the  $\beta\alpha$ -dibromocamphor into which  $\alpha\alpha$ -dibromo-

camphor is converted by the action of hydrogen bromide. If such a formula be adopted, we must regard the stability towards nitric acid which distinguishes *aa*-dibromocamphor from  $\alpha$ -bromocamphor and  $\beta\alpha$ -dibromocamphor as due to a shielding action consequent on the configuration of the molecule.

It is, unfortunately, not possible to decide between the formulæ



by subjecting *aa*-dibromocamphor to the action either of oxidising or of hydrolytic agents; the former are practically without action on it, nitric acid alone attacking it under the very special conditions described by Forster, and then in such a way as to throw no light on the problem here under discussion; and any attempt to hydrolyse it almost invariably leads to its reduction to monobromocamphor. On this account it appeared desirable to examine chlorobromocamphor, as it was to be expected that it would be possible, in the case of this compound, to study separately the behaviour of each of the halogen atoms. It was ultimately found that chlorobromocamphor, whether prepared from  $\alpha$ -chlorocamphor or from  $\alpha$ -bromocamphor, was an isomorphous mixture of two stereoisomerides, both of which gave one and the same  $\alpha$ -chlorocamphor on reduction. Moreover, crystallographic measurements showed it to be isomorphous with *aa*-dibromo- and *aa*-dichloro-camphor, and hence there can be no doubt that the three compounds are represented by the formulæ



To judge from the manner in which it is formed, it appears probable that tribromocamphor has its three bromine atoms in the  $\alpha\alpha'$ - and  $\beta$ -positions, as shown by the formula  $\text{C}_8\text{H}_{13}\text{Br} \begin{array}{c} \text{CBr}_2 \\ | \\ \text{CO} \end{array}$ . So too the

dibromochlorocamphor described in this paper must be regarded as having the formula  $\text{C}_8\text{H}_{13}\text{Br} \begin{array}{c} \text{CClBr} \\ | \\ \text{CO} \end{array}$ ; this formula is completely

established by the fact that the substance is an isomorphous mixture of two isomerides, which is both proof of the presence of the group

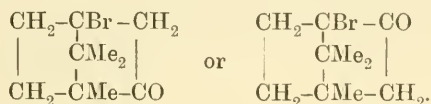
$\begin{array}{c} \text{Cl} \\ | \\ \text{C} \begin{array}{c} \diagup \\ \text{Br} \end{array} \\ | \\ \text{CO} \end{array}$  in the molecule, and evidence that the isomeric change

brought about by the action of hydrogen bromide does not affect the position of the chlorine atom.

The only points that now remain to be ascertained in order to solve the question of the constitution of the derivatives of camphor contain-



ing halogen, are, first, the location of the  $\beta$ -position in the molecule, and, secondly, the point at which substitution takes place when camphor is treated with hypobromous and hypochlorous acids—if indeed isomerides of the ordinary  $\alpha$ -modification are produced by such a method. It is at least possible that these two positions are identical, and coincide with the position occupied by the tertiary hydrogen atom in Bredt's formula, thus



### EXPERIMENTAL.

#### *$\alpha\alpha$ -Chlorobromocamphors.\**

*Preparation.*—At the outset of the inquiry, my attention was called by Dr. Armstrong to the great difference between the bromochlorocamphor obtained by merely warming a mixture of  $\alpha$ -chlorocamphor and bromine in molecular proportions, and the chlorobromocamphor formed by passing chlorine into fused  $\alpha$ -bromocamphor, heated on a water bath, until the required increase in weight is obtained: whereas the former crystallises magnificently, the latter is most difficult to obtain in well-defined forms. Attempts were first made to chlorinate bromocamphor by Dr. Armstrong's method, but in each of the five attempts an oil was obtained which did not crystallise even at the end of several months; in some cases, a little unchanged monobromocamphor separated from the oil, but nothing further.

A crystalline product was, however, obtained by heating  $\alpha$ -bromocamphor with sulphuryl chloride (1 mol.) in sealed tubes at about  $130^\circ$  during 6 hours. After draining the crystals from the oil and crystallising twice from methylated spirit, the substance was obtained in colourless crystals melting at  $56^\circ$ . The halogen was estimated by Carius's method,

0.1553 gave 0.1945 silver haloid. Halogen = 43.64.

0.1015 „ 0.1271 silver haloid. Halogen = 43.63.

$\text{C}_{10}\text{H}_{14}\text{ClBrO}$  requires halogen = 43.46 per cent.

The substance was found to be dextrorotatory,  $[\alpha]_D = 25.7^\circ$  in chloroform solution.

*Fractionation.*—As the melting point and rotatory power were changed by recrystallisation, an attempt was made to obtain constant

\* In order to avoid confusion, the name 'chlorobromocamphor' is used throughout this paper to represent 'chlorinated bromocamphor,' and, conversely, the name 'bromochlorocamphor' is used for a 'brominated chlorocamphor.'

values to compare with those for  $\alpha\alpha$ -bromochlorocamphor prepared by the action of bromine on chlorocamphor. For this purpose, a fresh quantity of the substance was prepared, and after being crystallised twice from spirit, was then submitted to a long series of crystallisations, without, however, reaching a point at which the rotatory power remained constant. Thus, it was found that

After 5 crystallisations	$[\alpha]_D = 21.7^\circ$
„ 7 „	$[\alpha]_D = 19.7^\circ$
„ 15 „	$[\alpha]_D = 11.6^\circ$
„ 24 „	$[\alpha]_D = 10.3^\circ$

Six different solvents were used for the fractionation, and in determining the specific rotatory power a 10 per cent. chloroform solution\* was used throughout, and the temperature kept as nearly as possible at  $20^\circ$ , in order to secure uniform conditions. Although a constant value for  $[\alpha]_D$  was not obtained, the change was very slow towards the end of the fractionation, and it is probable that the minimum value is not much below  $[\alpha]_D = 10^\circ$ .

No attempt was made to obtain a corresponding maximum value for  $[\alpha]_D$ , but a fraction of higher rotatory power was obtained from the mother liquors of the fractionation for which  $[\alpha]_D = 28.3^\circ$  (10 per cent. chloroform,  $15^\circ$ ).

The initial rotatory power of the substance is fairly constant. Three separate preparations, when crystallised twice from spirit, gave

- (1)  $[\alpha]_D = 25.7^\circ$  (6.42 per cent.  $\text{CHCl}_3$ ,  $21^\circ$ ).
- (2)  $[\alpha]_D = 26.2$  (10 „ „  $\text{CHCl}_3$ ,  $16^\circ$ ).
- (3)  $[\alpha]_D = 25.9$  (9.16 „ „  $\text{CHCl}_3$ ,  $25^\circ$ ).

The melting point is much less sharply defined, and until the substance has been crystallised a large number of times, it is neither sharp nor constant, and it was noticed that a higher value was obtained when the substance had been crystallised from chloroform than from other solvents. It melted initially at  $55^\circ$ , after one crystallisation from chloroform at  $58^\circ$ , and after 24 crystallisations both sharply and constantly at  $61^\circ$ . The change of melting point is therefore much less marked than that of specific rotatory power, and amounts to only  $3^\circ$  for 20 crystallisations.

A check analysis of the least soluble fraction showed that it had the normal composition of a chlorobromocamphor.

0.1017 gave 0.1264 silver haloid. Halogen = 43.33.

$\text{C}_{10}\text{H}_{14}\text{ClBrO}$  requires halogen = 43.46 per cent.

\* Throughout this paper, the phrase "10 per cent. chloroform" is used as an abbreviation for 'a solution in chloroform containing 10 grams in 100 c.c.'

*Crystallography.*—The substance was examined crystallographically, in order to determine to which series of di-derivatives of camphor it belongs. It crystallises in simple forms belonging to the orthorhombic system; the results of the examination of the crystals are given below.

*System.*—Orthorhombic.

*Axial Ratios.*— $a : b : c = 1.5338 : 1 : 1.9020$ .

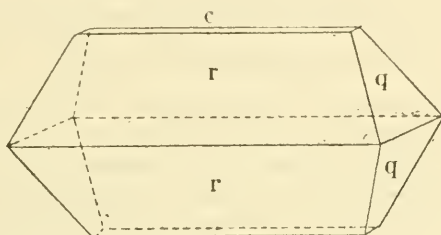
*Habit.*—From alcohol, ethylic acetate, &c., in short prisms elongated along the  $b$ -axis. From ether and chloroform in six-sided plates, flattened parallel to the face  $\{101\}$ .

*Forms present.*— $c = \{001\}$ .

$r = \{101\}$ .

$q = \{011\}$ .

FIG. 1



*Angles observed*—

Angle.	Number of observa- tions.	Limits.	Mean.	Calculated.
$r : r \ (101) : (\overline{1}0\overline{1})$	19	$77^{\circ}35'$ to $78^{\circ} 0'$	$77^{\circ}43'$	$77^{\circ}43'$
$r : r \ (101) : (\overline{1}01)$	19	$102 4$ „ $102 37$	$102 17$	—
$r : c \ (101) : (001)$	6	$50 56$ „ $51 20$	$51 8$	$51 8$
$q : q \ (011) : (0\overline{1}\overline{1})$	10	$124 30$ „ $124 45$	$124 37$	—
$q : q \ (011) : (0\overline{1}1)$	13	$54 57$ „ $55 39$	$55 21$	$55 23$
$q : c \ (011) : (001)$	9	$62 8$ „ $62 32$	$62 19$	$62 19$
$r : q \ (101) : (011)$	13	$73 1$ „ $73 23$	$73 12$	$73 3$
$r : q \ (101) : (0\overline{1}\overline{1})$	13	$106 37$ „ $106 59$	$106 47$	$106 57$

*Cleavage.*—No definite planes of cleavage.

*Optical Properties.*—The optic axial plane is the plane  $\{010\}$ , the optic axes emerging nearly perpendicular to the faces of the form  $r \{101\}$ . The  $a$ -axis is therefore the acute bisectrix, and the optic axial angle is about  $78^{\circ}$ . The double refraction is positive.

A comparison of the axial ratios with those given in the table on p. 574, shows very clearly that it belongs to the  $aa$ -series; the axial ratios being intermediate between those of  $aa$ -dibromo- and  $aa$ -dichloro-crystals and almost identical with the values given by Cazeneuve for  $aa$ -bromochlorocamphor.

*Reduction.*—When chlorobromocamphor is warmed with alcohol and

potash, a very vigorous action takes place, the solution becomes dark coloured, and inorganic potassium salts are precipitated; the solution is then diluted with water, and the insoluble precipitate drained off and distilled in a current of steam. When crystallised three times from spirit, the product melted sharply at  $92^{\circ}$  and its specific rotatory power was  $[\alpha]_D = 96.8^{\circ}$  (5.5 per cent. spirit,  $22^{\circ}$ ). On analysis,

0.1400 gave 0.1081 AgCl. Cl = 19.01.

$C_{10}H_{15}ClO$  requires Cl = 19.09 per cent.

The product of reduction is therefore identical with  $\alpha$ -chlorocamphor prepared from camphor, which melts at  $93^{\circ}$  and has a specific rotatory power  $[\alpha]_D = 95.8^{\circ}$  (5 per cent. spirit,  $20^{\circ}$ ).

*Theoretical.*—The preparation of chlorobromocamphor from  $\alpha$ -bromocamphor and its reduction to  $\alpha$ -chlorocamphor afford a complete proof that it is an  $\alpha$ -chlor- $\alpha$ -bromocamphor,  $C_8H_{14} \begin{smallmatrix} < \\ \text{CO} \end{smallmatrix} \begin{smallmatrix} \text{CClBr} \\ \text{CO} \end{smallmatrix}$ , and the other

members of the  $\alpha\alpha$ -series of di-derivatives of camphor containing halogens must, therefore, be similarly constituted.

Chlorobromocamphor is shown by its behaviour on fractionation to be a mixture of two isomeric substances differing widely in rotatory power. It is not, however a mixture of optical isomerides, such as is produced on sulphonation of chlorocamphor (Kipping and Pope, *Trans.*, 1897, 71, 962), for on reduction both constituents yield dextro-chlorocamphor of normal rotatory power. The only other isomerism possible for an  $\alpha\alpha$ -chlorobromocamphor is the stereoisomerism discussed in the earlier part of this paper.

A complete separation of the two stereoisomerides was not effected, but the less soluble constituent was probably obtained almost pure; this is the form of low rotatory power, in which the chlorine atom is in the  $\alpha$ -, and the bromine in the  $\alpha'$ -position, and we may therefore describe it as  $\alpha$ -chlor- $\alpha'$ -bromocamphor, m. p.  $61^{\circ}$ ,  $[\alpha]_D = 10^{\circ}$  (chloroform).

#### *$\alpha\alpha$ -Bromochlorocamphors.*

*Preparation.*— $\alpha\alpha$ -Bromochlorocamphor, prepared by adding one molecular proportion of bromine to  $\alpha$ -chlorocamphor heated on a water bath, was crystallised twice from spirit, and a quantity of about 100 grams was submitted to a series of recrystallisations in order to obtain constant values for the melting point and specific rotation. The product used for the fractionation melted at  $53$ – $55^{\circ}$ , and its specific rotatory power was  $[\alpha]_D = 51^{\circ}$ , (10 per cent. chloroform at  $14^{\circ}$ ); these values approximate to those given by Cazeneuve (*Bull. Soc. Chim.*, [ii], 1885, 44, 118) for the substance, namely, m. p.  $51.5^{\circ}$ ,  $[\alpha]_D = 51^{\circ}$ . The halogens were estimated by Carius's method:

0.1553 gave 0.1945 silver haloid. Halogen = 43.62.  
 0.2062 „ 0.2580 silver haloid. Halogen = 43.59.  
 $C_{10}H_{14}ClBrO$ , requires halogen = 43.46 per cent.

The specimen completely volatilised with steam, leaving no residue in the distilling flask.

*Fractionation.*—The substance was crystallised 26 times successively from six different solvents, and it was found that the specific rotatory power fell continuously, as is shown in the following table.

After 2 crystallisations	$[a]_D = 51.0^\circ$	(10 per cent. $CHCl_3$ , $14^\circ$ ).
„ 3	„ $[a]_D = 44.6$	(10 „ „ $15^\circ$ ).
„ 5	„ $[a]_D = 42.1$	(10 „ „ $15^\circ$ ).
„ 7	„ $[a]_D = 39.3$	(10 „ „ $15^\circ$ ).
„ 8	„ $[a]_D = 34.2$	(10 „ „ $16^\circ$ ).
„ 11	„ $[a]_D = 29.0$	(10 „ „ $20^\circ$ ).
„ 17	„ $[a]_D = 19.8$	(10 „ „ $20^\circ$ ).
„ 26	„ $[a]_D = 16.0$	( 9.2 „ „ $20^\circ$ ).

The melting point was raised to  $58^\circ$  by one crystallisation from chloroform, and the ultimate product melted sharply at  $61^\circ$ , melting just before the ultimate product from chlorobromocamphor when heated side by side with it. A check analysis showed it to have the normal percentage of halogen :

0.0944 gave 0.1182 silver haloid. Halogen = 43.63 per cent.

The minimum value obtained for the specific rotatory power was higher than in the case of chlorobromocamphor, but the large quantity of material available, and the high initial value of the specific rotatory power rendered it possible to obtain a much more pronounced maximum in this case. Several crops of crystals were taken from the chloroform liquors obtained in the first stage of the fractionation, and the residue, amounting to less than 5 per cent. of the whole, was distilled in a current of steam and crystallised from dilute spirit. The product melted at  $55^\circ$ , and had a specific rotatory power  $[a]_D = 63.9^\circ$  (7.02 per cent. chloroform,  $20^\circ$ ). The halogens were determined :

0.1016 gave 0.1259 silver haloid. Halogen = 43.18.

0.1597 „ 0.1977 silver haloid. Halogen = 43.13.

Calculated : halogen = 43.46 per cent.

*Stability.*—Attempts were made to obtain a complete conversion into one stereoisomeride by the action of heat and by the action of acids. A specimen, for which  $[a]_D = 48.8^\circ$  (10 per cent. chloroform,  $20^\circ$ ), after being heated at  $220^\circ$  for some time until it had become dark coloured, was distilled in a current of steam and crystallised from spirit, when its specific rotatory power was  $[a]_D = 46.8^\circ$  (5.41 per cent.



chloroform,  $21^{\circ}$ ). There is thus no change beyond that produced by the crystallisation. A second quantity was heated at  $100^{\circ}$  for 20 hours with a mixture of acetic and hydrochloric acids, but here again no change in specific rotatory power was observed beyond that due to the subsequent crystallisation of the product. The stability of the isomeric chlorobromocamphors is in marked contrast with the instability of  $\alpha'$ -bromocamphor and  $\alpha'$ -chlorocamphor. Thus the second bromocamphor described by Marsh was for the most part converted into  $\alpha$ -bromocamphor by distillation, and the action of acids and of alkalis is sufficient to secure the production of  $\alpha$ -bromocamphor as sole product in the bromination of camphor.

*Reduction.*—Bromochlorocamphor is readily reduced, either by alcohol and potash, or by zinc and acetic acid, the sole product being  $\alpha$ -chlorocamphor: when distilled in a current of steam, and crystallised twice from spirit, it melted at  $93^{\circ}$ , and two determinations of the specific rotatory power gave  $[\alpha]_D = 96.1^{\circ}$  (4.59 per cent. spirit,  $21^{\circ}$ ) and  $[\alpha]_D = 95.5^{\circ}$  (6.01 per cent. spirit,  $18^{\circ}$ ). The product of the action of zinc and acetic acid, precipitated with water and crystallised twice from acetic acid, gave  $[\alpha]_D = 95.4$  (2.85 per cent. spirit,  $15^{\circ}$ ).

The formation of  $\alpha$ -chlorocamphor as the sole product of reduction from bromochlorocamphor, which consists principally of  $\alpha'$ -chloro- $\alpha$ -bromocamphor, is a striking proof of the instability of  $\alpha'$ -chlorocamphor, both in acid and in alkaline solution.

*Theoretical.*—It has already been stated that bromochlorocamphor is isomorphous with chlorobromocamphor, and must, therefore, be similarly constituted. The same arguments are then available to show that it is an isomorphous mixture of the two forms of  $\alpha$ -chloro- $\alpha$ -bromocamphor. This conclusion is confirmed by a number of other observations.

(1) The less soluble constituents from bromochlorocamphor and from chlorobromocamphor must be regarded as being identical, for the last fraction in each case melted at  $61^{\circ}$ , and the specific rotatory power, which differed initially by  $25^{\circ}$ , approached within  $6^{\circ}$  of each other. Again, a specimen of chlorobromocamphor after 7 crystallisations had exactly the same specific rotatory power,  $[\alpha]_D = 19.8^{\circ}$ , and the same melting point as a specimen of bromochlorocamphor after 17 crystallisations. This affords a further proof of the identity of the two substances, and therefore of the constitution of bromochlorocamphor.

(2) When bromine acts on  $\alpha$ -chlorocamphor, a mixture of isomerides is produced, whereas by acting on  $\alpha$ -bromocamphor with bromine under similar conditions a single substance is produced. This renders it probable that the two isomerides in the former case differ only in that the positions of the chlorine and bromine atoms are interchanged, for the isomerism no longer exists when the two halogens are iden-



*Stereoisomeric Dibromochlorocamphors.*

On heating chlorocamphor with excess of bromine in sealed tubes, a *β*-dibromochlorocamphor is obtained, which has been found to be an isomeric mixture similar to the bromochlorocamphor obtained by the action of bromine on chlorocamphor at 100° and at atmospheric pressure.

*Preparation.*—The conditions under which it was prepared were similar to those followed in the case of *β*-bromochlorocamphor, the only noticeable difference being that the tubes used were somewhat larger. Eight sets of four tubes, each containing 6 grams of chlorocamphor and 5 c.c. of bromine, were heated for about 5 hours at temperatures ranging from 100° to 140°, and in each case the product isolated was dibromochlorocamphor, although two tubes containing equal charges of chlorocamphor and of bromine and heated for 5 hours at 120° had previously given *β*-bromochlorocamphor. The crude product is freed from bromine and from hydrogen bromide by passing a current of steam through it, and is subsequently freed from oil by draining on a filter pump; by crystallising three times from spirit, it is obtained in needle-shaped crystals melting at 78°. The yield amounts to about one-third of the weight of chlorocamphor used. The substance is very soluble in chloroform, somewhat less so in benzene, readily in light petroleum, acetic acid and spirit when hot, but only slightly when cold, and only dissolves with difficulty in light petroleum.

*Fractionation.*—When crystallised from spirit (three times), acetic acid, chloroform, and spirit, the substance melted at 81° and had the specific rotatory power  $[\alpha]_D = 44.5^\circ$  in a 5 per cent. solution in chloroform at 14°. On analysis by Carius's method,

0.2736 gave 0.4102 silver haloid. Halogen = 56.41.

0.3708 „ 0.5570 silver haloid. Halogen = 56.51.

$C_{10}H_{13}ClBr_2O$  requires halogen = 56.72 per cent.

When further crystallised from chloroform, benzene, light petroleum, acetic acid, and spirit, the specific rotatory power was raised to  $[\alpha]_D = 51.3^\circ$  for a 5 per cent. solution in chloroform at 19°. This is the maximum value, as after 23 crystallisations it was still found to be  $[\alpha]_D = 51.2^\circ$  for a 5 per cent. solution in chloroform at 16°. The melting point also becomes constant at 84°.

*Theoretical.*—Dibromochlorocamphor resembles the chlorobromocamphor already described in that the melting point and specific rotatory power are changed by recrystallisation, even after the removal of all impurities. From the method used in its preparation, it is probable that it contains bromine atoms in the *β*- and *α*-positions, and its behaviour shows it to be an isomorphous mixture of the two forms

which are possible for  $\beta\alpha\alpha$ -dibromochlorocamphor, as represented by the formulæ



The influence of the additional  $\beta$ -bromine atom is seen in three respects. (1) The solubilities of the isomerides show a greater difference than in the previous cases, allowing of a more ready separation of the two forms. (2) The relative solubility of the two forms is here reversed, the form of high rotatory power derived from  $\alpha$ -brom- $\alpha'$ -chlorocamphor being the less soluble, so that the rotatory power of the mixture increases on recrystallisation. (3) Only a relatively small amount of the more soluble isomeride is obtained in the crystals, the change of rotation observed being only  $7^\circ$ , as compared with  $16^\circ$  and  $30^\circ$  in the previous cases. The form of high rotatory power isolated by fractionation, is  $\beta\alpha$ -dibrom- $\alpha'$ -chlorocamphor, corresponding with the first of the formulæ given above, and this has therefore been obtained in a pure state; m. p.  $84^\circ$ ,  $[\alpha]_D = 51.3^\circ$  (5 per cent. chloroform).

*Crystallography.*—Dibromochlorocamphor crystallises from light petroleum, on spontaneous evaporation of the solvent, in short prisms, with extremely bright faces. These were examined, with the following results.

*System.*—Orthorhombic.

*Axial Ratios.*— $a : b : c = 1.4627 : 1 : 2.1332$ .

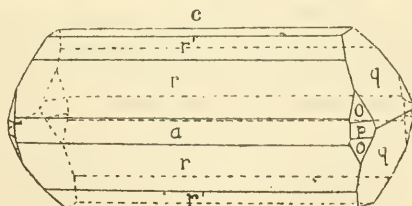
*Habit.*—Usually crystallises in prisms elongated along the  $b$  axis, but sometimes in plates flattened parallel to  $\{100\}$  or  $\{101\}$ .

*Forms present.*

$$\begin{array}{ll} a = \{100\} & q = \{011\} \\ c = \{001\} & p = \{110\} \\ r = \{101\} & o = \{111\} \\ r' = \{102\} & \end{array}$$

The pyramid form  $o = \{111\}$  is usually incomplete, and the prism form,  $p = \{110\}$ , only appears very occasionally.

FIG. 2.



*Angles observed.*

	Number of observations.	Limits.	Mean.	Calculated.
$a:r$ (100):(101)	31	$34^{\circ} 25'$ to $34^{\circ} 36'$	$34^{\circ} 30'$	—
$r:r'$ (101):(102)	29	19 21 „ 19 36	19 29	$19^{\circ} 28'$
$c:r'$ (001):(102)	28	35 54 „ 36 7	36 2	36 2
$a:r'$ (100):(102)	25	53 49 „ 54 8	53 59	53 8
$c:r$ (001):(101)	25	55 24 „ 55 38	55 30	55 30
$r:r$ (101):(10 $\bar{1}$ )	15	68 54 „ 69 10	69 1	69 0
$r':r'$ (102):(10 $\bar{2}$ )	13	71 58 „ 72 11	72 4	72 4
$q:c$ (011):(001)	31	64 46 „ 64 59	64 53	—
$q:q$ (011):(01 $\bar{1}$ )	15	50 9 „ 50 21	50 14	50 14
$c:p$ (001):(110)	10	89 51 „ 90 8	89 59	90 0
$q:r$ (011):(101)	21	75 58 „ 76 15	76 6	76 5
$q:r$ (011):(10 $\bar{1}$ )	17	103 49 „ 104 5	103 55	103 55
$q:r'$ (011):(102)	18	69 48 „ 70 3	69 56	69 56
$o:r'$ (111):(102)	9	52 49 „ 53 16	53 1	53 3
$q:o$ (011):(11 $\bar{1}$ )	5	57 1 „ 57 3	57 2	57 1
$a:q$ (100):(011)	26	89 50 „ 90 9	90 0	90 0
$q:o$ (011):(111)	15	31 31 „ 31 51	31 43	31 42
$o:a$ (111):(100)	16	58 6 „ 58 24	58 16	58 18
$o:r$ (111):(101)	3	50 25 „ 50 28	50 26	50 23
$o:r$ (111):(10 $\bar{1}$ )	3	129 30 „ 129 37	129 35	129 37
$c:o$ (001):(111)	14	68 46 „ 68 58	68 50	68 50
$o:p$ (111):(110)	6	21 10 „ 21 13	21 11	21 10
$o:o$ (111):(11 $\bar{1}$ )	4	42 21 „ 42 23	42 22	42 20
$p:a$ (110):(100)	3	55 21 „ 55 46	55 33	55 39
$r:p$ (101):(110)	2	62 20 „ 62 28	62 24	62 17
$p:q$ (110):(011)	2	41 16 „ 41 36	41 26	41 38

*Optic Axes.*—The optic axial plane is the plane {100}, the axis of  $a$  being the acute bisectrix. The double refraction is negative and the optic axial angle moderate.

*Cleavage.*—No definite planes of cleavage.

The crystallographic measurements of dibromochlorocamphor show that it forms the first member of a new series of derivatives of camphor containing halogen; the axial ratios resemble those of the  $\alpha\alpha$ -series much more nearly than those of the  $\beta\alpha$ -series, showing that these constants are more sensitive to substitution in the  $\alpha$ - than in the  $\beta$ -position. In most points it closely resembles  $\alpha\alpha$ -chlorobromocamphor, but the optic axial plane is here the plane {100} in place of the plane {001}, the  $a$ -axis being the acute bisectrix in both cases.



*αα-Dibromocamphor.*

In order to establish the conclusions drawn above as to the molecular structure of the chlorobromocamphors it was necessary to determine whether the corresponding *αα*-dibromocamphor is capable of being resolved into two constituents of unequal rotatory power. For this purpose a preparation of the substance was made, under conditions as far as possible similar to those used in the preparation of bromochlorocamphor, by warming *α*-bromocamphor with bromine (1 mol.), on a water bath. When crystallised three times from spirit, it melted sharply at 60°, and two determinations of the specific rotatory power gave  $[\alpha]_D = 40.0^\circ$  (10 per cent. chloroform, 21°) and  $[\alpha]_D = 40.1^\circ$  (10 per cent. chloroform, 20°). When further crystallised from chloroform, acetone, light petroleum, and spirit, it again melted sharply at 60°, and two determinations gave  $[\alpha]_D = 40.1$  (10 per cent. chloroform, 21°),  $[\alpha]_D = 40.2$  (10 per cent. chloroform, 20°). Dibromocamphor is therefore a homogeneous substance and is not an isomorphous mixture.

Dibromocamphor differs in a marked degree from most other camphor derivatives in that its specific rotatory power is almost independent of the solvent and of the strength of the solution. This is shown by the following determinations.

Solution.		$[\alpha]_D$ .	Temperature.
Chloroform	5 per cent.	40.0°	20°
"	10 "	40.1	20
"	20 "	40.1	20
Benzene	5 "	39.2	20
"	9 "	39.2	23
Spirit	5 "	39.2	14
Acetone	5 "	39.5	17
"	10 "	39.5	17
Ethyl acetate	10 "	39.1	17

From this it would appear that the influence of the solvent on the specific rotatory power in other cases is brought about either through the asymmetry of the *α*-carbon atom, or through the presence of a hydrogen atom, or a nitro-group in the *α*-position.

*βα-Bromochlorocamphor.*

This was prepared by heating *α*-chlorocamphor (6 grams) in a sealed tube with bromine (5 c.c.) for 5 hours at 120°. The product, after being washed with water and dilute soda and distilled in a current of steam, was drained on porous earthenware and crystallised from spirit.

When crystallised three times from spirit, it melted sharply at  $98^{\circ}$  and its specific rotatory power was  $[\alpha]_D = 69.8^{\circ}$  (5 per cent. chloroform,  $15^{\circ}$ ); when further crystallised from benzene and spirit, it again melted at  $98^{\circ}$ , and the value of  $[\alpha]_D$  was as before,  $69.8^{\circ}$ ; in a 5 per cent. benzene solution,  $[\alpha]_D = 42.0^{\circ}$  at  $15^{\circ}$ . Unlike  $\alpha\alpha$ -bromochlorocamphor, the isomeric  $\beta\alpha$ -compound is therefore a homogeneous substance.

A similar examination of  $\beta\alpha$ -dibromocamphor showed it to be a single substance melting at  $113^{\circ}$ ;  $[\alpha]_D = 100^{\circ}$  (5 per cent. chloroform,  $13^{\circ}$ ), and  $[\alpha]_D = 78^{\circ}$  (5 per cent. chloroform,  $13^{\circ}$ ).

Attempts to prepare a *tribromocamphor* by the action of bromine on  $\alpha$ -bromocamphor yielded only  $\beta\alpha$ -dibromocamphor, and no definite substance could be isolated from the product obtained by the action of bromine on  $\alpha\alpha$ -dibromocamphor.

In concluding this paper, I desire to express my thanks to Dr. Armstrong for the assistance he has so readily given me in the carrying out of this research, and in the preparation of this paper.

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## LX.—*Production of some Chloropyridinecarboxylic Acids.*

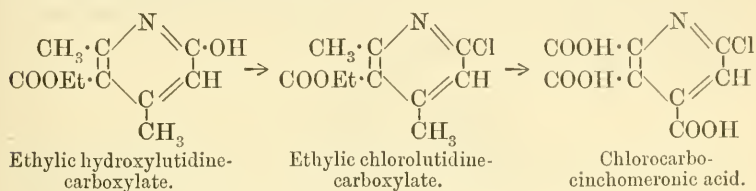
By J. NORMAN COLLIE, Ph.D., F.R.S., and W. LEAN, Redwood Research Scholar in the Research Laboratory of the Pharmaceutical Society of Great Britain.

AMONGST substituted pyridine compounds containing methyl or other hydrocarbon radicles (in the place of hydrogen), the hydroxy-derivatives, unfortunately, are unable to withstand the oxidising action of potassium permanganate, and, as a consequence, hydroxycarboxylic acids cannot be prepared by this means. A typical instance of this breaking down of the pyridine ring is that of methylpseudolutidostyryl, which yields methyloxamic acid when oxidised with potassium permanganate (Hantzsch, *Ber.*, 1884, 17, 1019). If, however, the hydroxy-group be replaced by chlorine, then the pyridine nucleus remains unbroken when boiled with potassium permanganate, and only the side groups are attacked with production of chlorocarboxylic acids of pyridine. The introduction of a methoxyl group also in certain cases seems to have the same effect as chlorine, for Freer and

Konigs (*Ber.*, 1885, 18, 2394), by the oxidation of methylamidocarbostyryl, obtained methoxypyridinedicarboxylate.

Various hydroxy- and chloro-carboxylic acids have already been investigated by one of the authors (*Trans.*, 1895, 67, 399; 1897, 71, 299, and 1897, 71, 653). The present communication is a continuation of the same work.

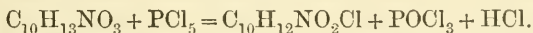
When ethylic acetoacetate is treated with gaseous ammonia, ethylic  $\beta$ -amidocrotonate is formed, and when the latter compound is saturated with hydrogen chloride and heated, it condenses to the ethylic salt of an hydroxylutidinecarboxylic acid. This pyridine derivative was used as the starting-point of the research. It was converted by means of phosphorus pentachloride into the corresponding chloro-compound, which in its turn was oxidised with potassium permanganate, giving a chlorinated tribasic acid.



Several intermediate ethers and salts also have been investigated, and the chlorocarbocinchomeronic acid has been reduced by means of tin and hydrochloric acid to the carbocinchomeronic acid itself.

#### *Ethylic Chlorolutidinecarboxylate.*

When the hydrochloride of ethylic amidocrotonate is heated, the chief product is an ethylic hydroxylutidinecarboxylate melting at 138—139°. This substance was treated, in quantities of about 20 grams at a time, with 24 grams of phosphorus pentachloride, and, on warming, the reaction takes place gradually, with evolution of hydrogen chloride.



It was found best to raise the temperature of the oil bath in which the mixture was heated to about 180°. After the action is over, the contents of the flask are poured into water, nearly neutralised with caustic soda, and the ether separated by distillation in a current of steam; the oil which passes over is dried and again distilled. It boiled at 288—290° (corr.), and on analysis it gave the following numbers.

Found C = 56.6; H = 6.0; N = 7.0; Cl = 16.6.

$\text{C}_{10}\text{H}_{12}\text{NO}_2\text{Cl}$  requires C = 56.2; H = 5.6; N = 6.5; Cl = 16.6 per cent.

This chloro-ether is an oily substance insoluble in water, and not



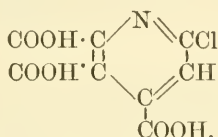
was obtained. In order to more effectually separate these acids, the whole was evaporated to dryness and treated with ethylic acetate, in which the acid of higher melting point was less soluble; by repeated treatment with this solvent, the mixture was ultimately separated into two acids, the less soluble, A, melting at  $212^{\circ}$  (corr.), and the more soluble, B, at  $169^{\circ}$  (corr.).

A, on analysis, gave the following results after drying at  $100^{\circ}$ .

Found C = 38.7 and 38.7; H = 1.8 and 1.7; N = 5.7; Cl = 14.7.

$C_8H_4NO_6Cl$  requires C = 39.0; H = 1.6; N = 5.7; Cl = 14.4 per cent.

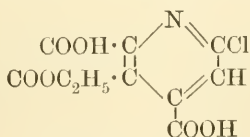
The crystalline acid contained  $2H_2O$ , for on drying at  $100^{\circ}$  it lost 15.1 per cent. Calculated for  $2H_2O$ ,  $H_2O = 14.4$  per cent. It was found, by titration with caustic soda, to be a tribasic acid, and therefore has the following formula.



Chlorocarbo-cinchomeric acid, m. p.  $212^{\circ}$ .

Unfortunately, when heated above its melting point, it charred completely, and fusion with potash also produced the same result. An aqueous solution of the neutral potassium salt gave a crystalline precipitate with barium chloride; a buff-coloured one with ferric chloride; with nitrate of silver, a precipitate of fine felted needles, and with ferrous sulphate, a deep orange coloration. The potassium salt, when concentrated, gave, with hydrochloric acid, a precipitate, not of the free acid, but of the acid potassium salt.

The more soluble acid, B, melting at  $169^{\circ}$ , seemed, from titration with caustic soda, to be a dibasic acid, and when boiled with excess of caustic soda alcohol was formed, and from the residue the acid A melting at  $212^{\circ}$  was obtained. From these results, it appeared probable that it was the monethylic salt of acid A. A chlorine determination was made. Found, Cl 13.1 and 12.9; calculated for  $C_{10}H_8NO_6Cl$ ; Cl = 13.0 per cent. Also, when in the crystalline condition, it was found to contain  $3H_2O$ . The acid potassium salt, already mentioned, was prepared by evaporating a solution of the neutral potassium salt to dryness with hydrochloric acid. This salt gave, on analysis, K = 12.7. Calculated for  $C_{10}H_7NO_6ClK$ , K = 12.5 per cent. The substance therefore has the following formula.



Compound B, m. p.  $169^{\circ}$ .



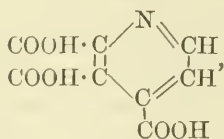
As the acid melting at  $212^{\circ}$  was a chlorocarbocinchomeric acid, the action of tin and hydrochloric acid on it was tried. A few grams of the acid were allowed to stand for some days with hydrochloric acid and excess of tin in a warm place; the tin was then precipitated with hydrogen sulphide, and when the filtrate was evaporated to dryness and the residue tested, it was found to contain an acid free from chlorine. This acid was very soluble in water, crystallising in small plates; and with ferric chloride, gave a blood-red coloration. It contained water of crystallisation, and when heated in a capillary tube it turned from about  $200^{\circ}$  and melted at  $250^{\circ}$  with complete decomposition. As we had only a small quantity of the acid, it was converted into the silver salt by precipitation of an aqueous solution of the free acid by means of silver nitrate. The silver salt thus prepared separated in needles, and after one recrystallisation, seemed pure. For analysis, it was dried at  $100^{\circ}$ .

Found, C=22.1; H=1.0; Ag=51.3 per cent.

$C_8H_3Ag_2NO_6$  requires C=22.5; H=0.7; Ag=50.8 per cent.

The silver salt was therefore the monacid silver salt of carbocinchomeronic acid,  $C_5H_2N(COOAg)_2 \cdot COOH$ , and the above mentioned properties of the acid agree well with those of carbocinchomeronic acid itself which melts at  $250^\circ$ . This acid was first obtained by the oxidation of quinine, and also from several of the cinchona alkaloids; but it has since been synthetically produced by several different reactions, from an  $\alpha\beta\gamma$ -lutidine by oxidation (Micheal, *Ber.*, 1885, 18, 2027), from methylchinolinic acid, from lepidine, &c.

Carbocinchomeric acid or pyridinetricarboxylic acid,



is one of the products of oxidation of quinine, cinchonidine, cinchonine, quinidine, and papaverine, and therefore its formation from ethylic acetoacetate is of some interest.

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# LXI.—*Molecular Weights in Solution of Permanganates, Perchlorates, and Periodates.*

By J. MURRAY CROFTS, B.A., B.Sc., Research Student of Emmanuel College.

It is well known that the salts of permanganic acid are generally isomorphous with those of perchloric acid. Until quite recently, the formula of the potassium salts was written for permanganic acid  $K_2Mn_2O_8$ , and for perchloric acid  $KClO_4$ , although the law enunciated by Mitscherlich in the early part of the century points to a similarity in the chemical constitutions of the two salts. Recent work, however, has indicated the correctness of the more simple formula  $KMnO_4$  for potassium permanganate.

## *Previous Work.*

*Perchlorates.*—Tammann (*Mém. Acad. Petersb.*, 1887, 35) gives the lowering of the vapour pressure of water produced by solution therein of various salts. For potassium perchlorate, he gets a value similar to that obtained for haloid salts of univalent metals, and Raoult (*Compt. rend.*, 1889, 107, 442) gives, for the lowering of the vapour pressure of alcohol by sodium perchlorate dissolved in it, a value which corresponds with the formula  $NaClO_4$ .

Oswald (*Lehrbuch*, II, 733), by the specific conductivity method gets  $\Delta = \mu_{1024} - \mu_{32} = 13.6$  for potassium perchlorate, the value of  $\Delta$  for the simple salts of monobasic acids being about 10.

*Permanganates.*—The work done on the molecular weights of permanganates in solution deals only with the specific conductivity of the salts. Bredig (*Zeit. physikal. Chem.*, 1893, 12, 233), using the potassium salt, got a fairly good value for the formula  $KMnO_4$  ( $n = \text{basicity} = 0.93$ ). Franke (*Zeit. physikal. Chem.*, 1895, 16, 475) gives the results of a series of experiments on the specific conductivities of permanganates, but his values for  $\Delta$  vary between very wide limits, as shown in the following table, where the figures given are the means of the values obtained by Franke for each salt.

Ag = 6.4	$\frac{1}{2}Sr = 9.3$
Na = 8.4	$\frac{1}{2}Ca = 14.5$
Li = 13.4	$\frac{1}{2}Ba = 19.7$

It seemed worth while, therefore, to make further investigations on this subject, and it was determined to use, if possible, Raoult's freezing point method, a method which apparently had not been used before for these salts.

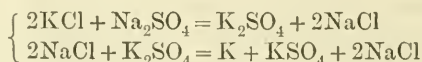
The preparation of pure potassium permanganate and potassium perchlorate offered little difficulty, the salts being purified by repeated crystallisation and the purity tested by analyses.

Very many substances were tried as solvents for these salts, potassium perchlorate, however, is very insoluble; it is soluble to a very small extent in a few organic solvents (absolute alcohol 0.1 per cent., benzene 0.2 per cent., at the boiling point of the solvents).

As regards potassium permanganate, it was found that, although this salt is fairly soluble in many substances, such as alcohol, acetone, and pyridine, oxidation by the permanganate soon took place, and no suitable solvent could be found.

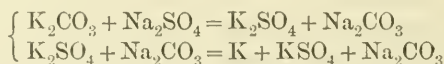
It was at this point that my attention was drawn to a paper by Löwenherz (*Zeit. physikal. Chem.*, 1895, 18, 70), who had used Glauber's salt as his solvent. The constant was obtained from experimental results with indifferent substances, and also theoretically by the method due to Van't Hoff, using the latent heat of fusion. Determinations of the molecular weights of sodium salts, such as the chloride and carbonate were then made, and the molecular depression showed that no dissociation took place when the salts were dissolved in melted Glauber's salt (compare the method of determining the vapour density of phosphorus pentachloride). With sulphates, potassium sulphate for example, a value for the constant was obtained double that of the ordinary value, as if  $K_2SO_4$  had split into K and  $KSO_4$ .

The molecular weights of salts containing other acidic and basic radicles could be determined by a consideration of the number of foreign substances which could be formed. With potassium chloride, for example, the following conditions are obtained.

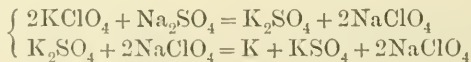


that is, 2 molecules of KCl give four foreign substances in solution.

Again,

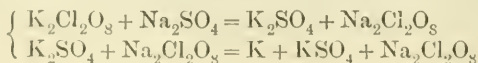


1 molecule giving three foreign substances with perchlorates or permanganates, then,



2 molecules giving four foreign substances.

If, however, the molecule of potassium perchlorate is  $K_2Cl_2O_8$ ,



that is, 1 molecule (the molecular weight being doubled) gives three foreign substances.

If sodium salts were used, a normal value of the constant must be obtained, as no dissociation could occur. In the present work, both sodium and potassium salts were used.

The preparation of pure sodium perchlorate presented little difficulty. It was prepared from the chlorate by heating (Serullas, *Ann. Chim. Phys.*, 1832, [ii], 46, 294, 323). The salt was purified by repeated crystallisation from alcohol.

The preparation of pure solid sodium permanganate was not so simple. No fuller account of its preparation could be found than that contained in Watt's Dictionary. An outlined account of the method adopted is as follows.

Silver permanganate was obtained from silver nitrate and potassium permanganate, and purified by recrystallisation (Dewar and Scott, *Proc. R. Soc.*, 35, 44). A weighed amount of these pure crystals was dissolved in hot water and treated with a little less than the calculated quantity of pure sodium chloride dissolved in a small quantity of water; the precipitated silver chloride was then filtered off and the solution evaporated down in a vacuum. Eleven grams of silver permanganate required roughly about 1 litre of hot water to dissolve it. The evaporation of the sodium permanganate solution was continued until the liquid was reduced to about 20 c.c.; this was placed in a glass dish in a vacuum over sulphuric acid, when it became solid in a few days. The mass, which was not definitely crystalline, but finely granular, was dissolved in a small quantity of cold water (to remove excess of silver permanganate), filtered through glass wool, and again placed in a vacuum. This time, large, beautiful crystals of the salt were obtained; these were again recrystallised. The crystals were free from chlorine and silver, and analyses showed them to be very nearly pure. The salt crystallises in the form of long needles (similar to those of the potassium salt) which contain water of crystallisation; they have the formula  $\text{NaMnO}_4 + 3\text{H}_2\text{O}$ . The water of crystallisation is driven off at the temperature of a steam oven; on exposure to the air, the crystals effloresce and decompose slightly.

"Pure" Glauber's salt was recrystallised and dried in the air to the approximate composition  $\text{Na}_2\text{SO}_4 + 10\text{H}_2\text{O}$ . It is not necessary that the composition of the crystals should exactly correspond with this formula, as water is driven off during the process of melting. The exact composition of the salt used must, however, be known; then from the amount of anhydrous sulphate deposited at the bottom of the Beckmann tube during the course of the experiment, the actual amount of melted Glauber's salt,  $\text{Na}_2\text{SO}_4 + 10\text{H}_2\text{O}$ , can be calculated. It is important to remove the water driven off and condensed on the

side of the tube, otherwise drops are liable to run down into the liquid, just as the solvent is freezing out, and so to vitiate the results of the reading.

The presence of anhydrous sulphate in the tube during an experiment ensures the saturation of the supernatant liquid with sodium sulphate.

Owing to the method of calculating the actual amount of solvent used, only determinations with one concentration can be done in each experiment. Care must be taken in the stirring to prevent the liquid and the deposited anhydrous sulphate cooling at different rates.

To the constant  $C$ , obtained by determining the molecular depression for indifferent substances, Löwenherz gives the value 32.6.

From the equations given above, if the formula for potassium perchlorate is  $\text{KClO}_4$ , the value for  $C = 65.2$ . If the formula is  $\text{K}_2\text{Cl}_2\text{O}_8$ ,  $C = 1/2 (32.6 \times 3)$ . (The figure is  $1/2 (32.6 \times 3)$ , because in the calculation the value for  $M$ , the molecular weight, is taken as  $138.6 = \text{KClO}_4$ ).

The results obtained, using both potassium and sodium salts, are tabulated below.

$G$  = Weight of solvent, in grams.

$F$  = Weight of substance introduced, in grams.

$\Delta$  = Depression of freezing point observed.

$C$  = Constant obtained.

In the formula  $C = \frac{MG\Delta}{100F}$ .

	$G$ .	$F$ .	$\Delta$ .	$C$ .
$\text{KClO}_4$	24.14	0.1225	0.257	2(34.7)
	23.68	0.1275	0.270	2(34.5)
	22.44	0.1570	0.350	2(36.0)
	22.10	0.1845	0.434	2(36.0)
$\text{NaClO}_4$	23.40	0.2080	0.200	28
	24.52	0.3055	0.292	29
	25.20	0.3880	0.345	28
$\text{KMnO}_4$	23.04	0.1853	0.276	2(27.5)
	25.85	0.1860	0.272	2(30.0)
	23.10	0.2043	0.307	2(27.5)
$\text{NaMnO}_4$	23.60	0.328	0.258	27.6
	22.81	0.344	0.290	28
	21.50	0.344	0.286	26

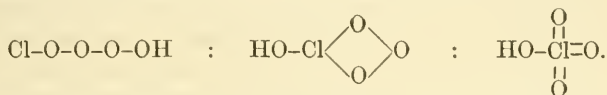
The values for the constant thus obtained give for perchlorates the formula  $\text{M}'\text{ClO}_4$ , and for permanganates the formula  $\text{M}'\text{MnO}_4$ .

These results help to justify the position of manganese in group VII in the periodic classification of the elements. The dioxide of manganese is acidic, forming the so-called manganites, of which  $\text{CaO}, \text{MnO}_2$



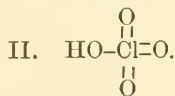
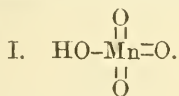
is well known. The trioxide,  $\text{MnO}_3$ , is the anhydride of manganic acid,  $\text{H}_2\text{MnO}_4$ . The anhydride of permanganic acid, namely,  $\text{Mn}_2\text{O}_7$ , can also be obtained. Manganese, then, has decidedly acidic properties. The results of the present work emphasise the analogy between manganese and chlorine.

Various formulæ have been suggested for perchloric acid.



In the first, upheld by Blomstrand (*Ber.*, 1883, 16, 183), the chlorine atom functions as a monad; in most of its compounds, the chlorine atom is univalent. The evidence in favour of the second formula, in which the chlorine atom, represented as trivalent, is not very strong, there is the hypothetical oxide,  $\text{Cl}_2\text{O}_3$ , and its acid,  $\text{HClO}_2$ . Also the halogen atoms certainly function as triads in compounds such as  $\text{ICl}_3$ .

The third formula, in which the chlorine atom is represented as septavalent, is upheld by Spring (*Bull. Acad. Belg.*, [ii], 39, 887). In Mendeléeff's classification, chlorine and manganese are placed in group VII, the typical oxides of which are of the form  $\text{R}_2\text{O}_7$ . Manganese heptoxide is known, and its acid must be represented by the formula  $\text{HMnO}_4$ , in which the manganese atom is probably a heptad, and hence the constitutional formula must be that represented by I.



Although the heptoxide of chlorine,  $\text{Cl}_2\text{O}_7$ , is unknown, the well-marked analogy between manganese and chlorine points to a similar formula, II, for perchloric acid.

These formulæ can represent, in a simple fashion, all the various reactions of the compounds.

*Addendum.*—I have been fortunate in obtaining some pure potassium periodate, which was prepared by Dr. Kimmins some time ago (*Trans.*, 1889, 55, 148); by estimation of the potassium, the salt was shown to be pure metaperiodate,  $(\text{KIO}_4)_x$ . The molecular weight of this was determined by the method described above. The value of the constant obtained was  $2 \times 29$ , corresponding, therefore, with the formula  $\text{KIO}_4$ .

My best thanks are due to Mr. Pattison Muir for permitting me to work in his laboratory, and for the many facilities he has afforded me in my work.

## LXII.—*The ultraviolet Absorption Spectra of some closed Chain Carbon Compounds.*

By W. N. HARTLEY, F.R.S., and J. J. DOBBIE, M.A., D.Sc.

It has been shown by one of us that benzene, naphthalene, anthracene, and phenanthrene all yield spectra with characteristic absorption bands, that this property is shared by the various homologues of benzene, their hydroxyl, carboxyl, amido-, and other such derivatives, and by the tertiary bases pyridine, picoline, and quinoline.

It was, on the other hand, further shown that open chain carbon compounds, such as the paraffins and their derivatives, alcohols, aldehydes, acids, and ethereal salts, glycerol, and the sugars, gave no absorption bands; neither did the terpenes when free from benzenoid derivatives, nor substances of constitution similar to hexachlorobenzene or camphor. (Hartley and Huntington, *Phil. Trans.*, 1879, 170, 257. *Proc. Roy. Soc.*, 1880, 31, 1. Hartley, *J. Chem. Soc.*, 1881, 39, 153; 1882, 41, 45; 1885, 47, 685. *Phil. Trans.*, 1885, 176, 471.)

Accordingly, it was concluded that the grouping and linking of the carbon atoms, or of the carbon and nitrogen atoms, forming the nucleus of the compounds were the cause of the banded spectra, and the origin of the bands was accounted for.

With recent advances in organic chemistry, it has been considered desirable to continue these researches and extend the inquiry towards compounds of a new type, such as, for instance, closed chains wherein the carbon atoms, four or six in number, are singly linked, or two pairs are doubly linked, and to ascertain what effect oxygen and other polyvalent atoms as links in a closed chain may exert on the optical properties. As a commencement, we have examined furfuraldehyde and its derivatives, pyrrole,\* diketohexamethylene, and thiophen.

The general method of procedure previously followed has been adhered to. We state the mode of preparing the substances in as pure a condition as possible, and describe the spectra transmitted by solutions in various diacticinic solvents.

*Furfuraldehyde.*—The specimen, which was purchased from Messrs. T. & H. Smith & Co., of Edinburgh, was dried over calcium chloride, purified by fractional distillation at atmospheric pressure, and the fraction boiling at 159° again subjected to fractional distillation under a pressure of 124 mm., when the whole of the liquid, with the exception of a small residue, came over at constant temperature. The purified specimen had a very pale straw yellow colour, and boiled constantly at 161—161·5° (1-V.) Bar. = 764·9 mm.

\* This is the basic compound,  $C_4NH_5$ , to which the name pyrroline is given in this Journal.—EDITOR.



*Pyromucic Acid*, or *Furfurancarboxylic Acid*.—This was prepared by adding to 25 grams of furfuraldehyde an equal volume of alcoholic potash containing 200 grams of KOH per litre; the mixture became warm, and in a short time glistening brown or dark red crystals of potassium pyromucate separated. After about 12 hours, these were dissolved in water and the solution shaken thoroughly with ether to remove any furfuryl alcohol; the solution requires a considerable amount of ether for complete extraction.

The solution of potassium pyromucate thus obtained was mixed with sufficient strong hydrochloric acid to effect complete decomposition and to render the solution slightly acid, the precipitated pyromucic acid filtered off, and the filtrate agitated with ether to extract the remainder of the acid.

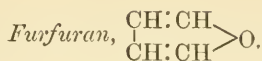
The pyromucic acid was purified by dissolving it in water, boiling with animal charcoal to decolorise it, filtering, concentrating, and allowing it to crystallise. The acid was obtained in colourless crystals, which melted at 132°.

*Pyromucic acid*,  $C_4H_3O \cdot COOH$ .

0.112 gram in 20 c.c. of alcohol. Strong general absorption, no absorption band.

Thickness of layer of liquid in millimetres.	Description of spectrum.	$\frac{1}{\lambda}$	$\lambda$
25	Feeble transmission with complete absorption of all rays beyond .....	3471	2881
20	The same beyond .....	3486	2868
15	The same, gradually increasing in strength but by no means strong.		
10			
5			
4			
3			
2	The same with complete absorption beyond.....	3639	2748
1			

*Furfuran*.—Prepared from barium pyromucate by distillation with soda-lime and condensing the distillate in the usual way, using U-tubes and a freezing mixture; the brown liquid which collected in the U-tubes was dried over calcium chloride and distilled from a water bath. The product, which boiled at 32°, was clear and colourless (Limpricht, *Ann.*, 1873, 165, 281).



I.—0.068 gram in 20 c.c. of alcohol. Strong general absorption, no bands.

Thickness of layer in millimetres.	Description of spectrum.	$\frac{1}{\lambda}$	$\lambda$
25	Spectrum weak, with fainter lines cut out between 2768 and .....	3638	2748
	All rays absorbed completely beyond .....	3638	2748
	Except a strong line visible at .....	3886	2573
20	The same, faint indication of line at.....	3740	2673
15	The same .....		
10	The same, faint indication of lines at 3793 and .....	4321	2314
5	Complete absorption beyond .....	4321	2314
	Very faint lines at 3743, 3768, 3795, 4057, 4300, 4315; stronger line at 4321; faint lines at 4340, 4375.		
4	Same as preceding with a few more faint lines visible between 3886 and 4321.		
3	Same as 4.		
2	Same as 3, except that a faint line appears at 4415 .....		2265
1	Same as preceding.		

### Furfuran.

II.—0.068 gram in 100 c.c. alcohol.

Thickness of layer in millimetres.	Description of spectrum.	$\frac{1}{\lambda}$	$\lambda$
5	Complete absorption beyond .....	4415	2265
	Transmission feeble between 3638 and 3886, and between 3886 and 4306.		
4 )	Same as 5.		
3 )			
2	Somewhat brighter than 3, feeble line at 4510.		
1	Same as preceding.		



## Furfuran.

III.—0.068 gram in 500 c.c. alcohol.

Thickness of layer in millimetres.	Description of spectrum.	$\frac{1}{\lambda}$	$\lambda$
4	Same as 1, II., except that a feeble line is visible at .....	4556	2194
3	Same, line more distinct at.....	4556	
2	The whole spectrum visible, including line at...	4650	2150
1	Same; somewhat stronger.		

*Diketohexamethylene*.—Powdered ethylic succinylsuccinate (10 grams) was added to concentrated sulphuric acid (42 c.c.) contained in a conical flask, and as there was no rise of temperature, the mixture was warmed slightly to obtain complete solution.

The solution was poured on to ice (145 grams) contained in a beaker, when a flaky, white, flocculent precipitate was formed without rise of temperature; the whole was placed in a flask of a litre capacity, alcohol (4 c.c.) added, and the liquid cohobated for about 9 hours, until all the solid matter had dissolved. By distilling off 50 c.c. of the solution, the alcohol was removed, and to the residue some calcined and powdered sodium carbonate was cautiously added so as to neutralise the acid. A pale blue precipitate formed which gradually darkened, and on adding dilute sulphuric acid this precipitate redissolved. The liquid, on being left overnight, deposited sodium sulphate, which was separated by filtration. To the filtrate, ammonium sulphate was added, and subsequently a large quantity of chloroform. The chloroform, after separation, was distilled off, and the solid residue dissolved in absolute alcohol, but the substance was difficult to crystallise owing to its low melting point. The alcoholic solution was therefore warmed and placed in a vessel over sulphuric acid, which was then exhausted; after a time, crystals separated which were filtered from the mother liquor, washed once with alcohol, and dried between filter paper. The crystals were colourless and melted at 78° (Baeyer *Ann.*, 1895. 278, 96).



0.112 gram in 20 c.c. of alcohol.

Thickness of layer of liquid. in millimetres.	Description of spectrum.	$\frac{1}{\lambda}$	$\lambda$
25	Spectrum transmitted fairly strongly to ..... but very feebly beyond. There is a feeble transmission of the strongest cadmium lines at 2638, 3886, and 4290, which shows that the absorption is weak throughout, although continuous.	3239	3087
20	The same, but more strongly to..... A line appears faintly at 3353.	3239	3087
15	The same.		
10	The same, a line appears faintly at 3470, very faintly at 3529, and a feeble continuous spectrum runs right through.		
5	The same, with the feeble continuous spectrum somewhat stronger but not quite distinct extending to the extreme end.....	4290	2331

*Pyrrole*.—The specimen employed, which was purchased from Schuchardt, was distilled in a darkened room, as the substance decomposes readily in sunlight. Three fractions were obtained; the second, which was the larger part of the whole, boiled between 129° and 130°. It was re-distilled in the dark, and the clear, colourless liquid obtained boiled between 129° and 130° as before. This was then subjected to distillation under a pressure of 150 mm., when it all came over at constant temperature. The boiling point was 130.5° (i. V.) under a pressure of 764.75 mm.



I.—0.067 gram in 20 c.c. of alcohol. Strong general absorption, but no absorption band.

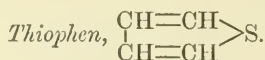
Thickness of layer of liquid in millimetres.	Description of spectrum.	$\frac{1}{\lambda}$	$\lambda$
25 } 20 }	Absorption complete beyond ..... with the exception of a strong cadmium line just faintly visible at .....	3893 3915	2568 2554
15 } 10 }	Absorption complete beyond .....	4027	2483
5 } 4 }	" " " .....	4087	2446
3 } 2 } 1 }	Extension of the transmitted spectrum to ..... Absorption beyond this.	4165	2400

## II.—0.067 gram in 100 c.c. of alcohol.

Thickness of layer of liquid in millimetres.	Description of spectrum.	$\frac{1}{\lambda}$	$\lambda$
5 } 4 } 3 } 2 }	Continuous spectrum extends to.....	4202	2379
	“ “ “ .....	4290	2331

*Thiophen.*—This was purchased from Schuchardt, and purified by fractional distillation. The middle fraction, by far the greater part of the whole, was a clear, colourless liquid boiling at 84–85°. It was re-distilled under a pressure of 140 mm., when it all came over at a constant temperature. The boiling point was found to be 84.5° (i. V.). Bar. 763.56 mm.

This substance has more recently been examined by J. Pauer, who found that its vapour gave a continuous absorption to  $\lambda 2460$ , whilst the liquid pressed into a film between quartz plates gave an absolute absorption to  $\lambda 2540$  (*Ann. Phys. Chem.*, 1897, 61, 363, “Absorption ultraviolet Strahlen durch Dämpfe und Flüssigkeiten”). Thiophen might still show an absorption band on dissolving and diluting the solution, but our examination of the spectra under these conditions proved that there was no selective absorption.



Remarkable for its very strong general absorption, but no absorption band. It was necessary to take a series of five plates, and to use very dilute solutions.

## I.—0.084 gram in 20 c.c. of alcohol.

Thickness of layer of liquid in millimetres.	Description of spectrum.	$\frac{1}{\lambda}$	$\lambda$
25 down to } 1 }	Absolute absorption beyond .....	3886	2573
	Transmitted rays gradually extending to about	3915	2554

## II.—0.084 gram in 100 c.c.

Thickness of layer of liquid in millimetres.	Description of spectrum.	$\frac{1}{\lambda}$	$\lambda$
5 down to } 1 . }	Absolute absorption beyond .....	3949	2532
	” ” ” .....	4043	2473

## 0.084 gram in 500 c.c.

5 down to } 3 }	Absolute absorption beyond .....	4043	2473
2 down to } 1 }	” ” ” .....	4075	2454
	The strong lines of cadmium are feebly transmitted 4291 to .....	4656	2147

## Thiophen.

III.—0.084 gram in 20 c.c of alcohol. The exposure was doubled for this and IV, being raised from 15 to 30 seconds. This did not render the absorption less complete, but the transmitted rays being stronger, the absorption was very clearly marked.

Thickness of layer of liquid in millimetres.	Description of spectrum.	$\frac{1}{\lambda}$	$\lambda$
25 down to } 1 }	Absolute absorption beyond .....	3915	2554
	” ” ” .....	3979	2513

## IV.—0.084 gram in 100 c.c. of alcohol.

Thickness of layer of liquid in millimetres.	Description of spectrum.	$\frac{1}{\lambda}$	$\lambda$
5 down to } 1 }	Absorption absolute beyond .....	4020	2487
	” ” ” .....	4049	2469

## 0.084 gram in 500 c.c.

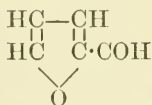
5 down to } 3 }	Absolute absorption beyond .....	4049	2469
2 and 1 }	” ” ” .....	4127	2423
	The very strong lines of cadmium are now feebly transmitted.		

V.—0.084 gram in 2500 c.c. of alcohol.

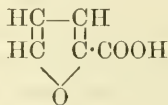
Thickness of layer of liquid in millimetres.	Description of spectrum.	$\frac{1}{\lambda}$	$\lambda$
5 and 4	Continuous spectrum transmitted to.....	4127	2423
3	Spectrum almost continuous but faint.		
2 and 1	Spectrum continuous to the cadmium line .....	4306	2322

The extraordinary absorption caused by thiophen is due to the sulphur it contains. This property is shared by carbon bisulphide, as is well known.

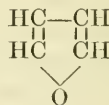
*Conclusions.*—It will be seen that, however intense the absorption of the ultraviolet rays may be, there is in no case any absorption band observed in substances with the following constitution; this is quite in accordance with previous observations, and might have been predicted.



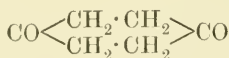
Furfuraldehyde.



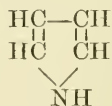
Pyromucic acid.



Furfurane.



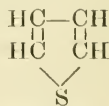
Diketohexamethylene.



Pyrrole.



Furfuramide.



Thiophen.

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### LXIII.—*Enantiomorphism.*

By FREDERIC STANLEY KIPPING and WILLIAM JACKSON POPE.

ENANTIOMORPHOUS substances are naturally divisible into two classes: (*a*) consisting of those compounds in which the enantiomorphism is determined by the structure of the chemical molecule, and (*b*) consisting of those crystalline substances of which the enantiomorphism is not inherent in the molecules, but is determined solely by their arrangement.



The first class (*a*) consists of all compounds containing what is usually called an asymmetric carbon atom. Such substances not only condition circular polarisation in the amorphous or liquid state, this being one mode of expression of the enantiomorphism, but as we have previously shown ("Racemism and Pseudoracemism," *Trans.*, 1897, 71, 989), they can only crystallise in one or other of the enantiomorphous crystalline systems; the latter form is merely a more precise statement of Pasteur's law, the truth of which has been questioned by Walden (*Ber.*, 1896, 29, 1692), but which, as we pointed out, stands or falls with the present theory of crystal structure. Furthermore, it can be shown that, in the crystallisation of a substance consisting of enantiomorphous chemical molecules, the resulting crystalline structure can only be of the one hand; that is to say, the crystals of a substance which is dextrorotatory in the amorphous state must be either right- or left-handedly enantiomorphous, but cannot be partly the one and partly the other.

To the second class (*b*) of enantiomorphous substances, namely, those in which the enantiomorphism is purely one of arrangement of the chemical molecules in the crystalline structure, belong compounds such as the cubic tetartohedral sodium chlorate and quartz; such substances, of course, are not optically active in the amorphous or liquid state, but they crystallise in enantiomorphous systems, and their crystals sometimes rotate the plane of polarisation, this being again one mode of expression of the enantiomorphism.

Now the crystallisation of a substance such as sodium chlorate, which does not consist of enantiomorphous molecules, is obviously a different process from that of the crystallisation of an optically active substance; whereas the latter must invariably give crystals which are either right- or left-handedly enantiomorphous, there is no *a priori* reason why the former should give crystals of the one hand in preference to those of the other. The average product of a large number of crystallisations of sodium chlorate from water should consist of 50 per cent. of crystals of each hand, because there is operative an equal tendency to deposit dextro- and lævo-sodium chlorates. The only quantitative data bearing on this point with which we are acquainted are those obtained by Landolt (*Ber.*, 1896, 29, 2404), who has determined the specific rotation of the crystalline powder of sodium chlorate, deposited from a pure aqueous solution, by examining it polarimetrically whilst suspended in a liquid of approximately the same refractive index; Landolt showed that, taken collectively, the sodium chlorate crystals were inactive, although each individual was either right- or left-handed. Gernez (*Compt. rend.*, 1868, 66, 833) also states that on crystallising an aqueous solution of sodium chlorate, it yields "des

poids à peu près égaux de cristaux des deux espèces"; no statistics of weight or number of crystals, however, are given.

The question of the proportion in which enantiomorphously related crystals are deposited in the case of such substances is one of prime importance for various reasons: firstly, because observations with which we deal below are on record to the effect that the proportion is not that of unity; and, secondly, because it is necessary for our present purpose that the proportion should be accurately determined, since we show in this paper that the proportion can be varied by bringing to bear a suitable enantiomorphous or directive influence during crystallisation. We have, therefore, examined the crystals of sodium chlorate deposited from pure aqueous solutions in order to determine whether the ratio of dextro- to lævo-sodium chlorate is that of unity; since, however, Landolt's method was not applicable to the development of the work on the lines we proposed, we had to adopt a somewhat different mode of procedure. Instead of showing, as Landolt did, that the weights of the two enantiomorphously related forms of sodium chlorate deposited are equal, we show that the crystals of each kind deposited are, on the average, the same in number.

The method used was as follows. About 200 c.c. of a saturated aqueous solution of sodium chlorate was put into a shallow glass crystallising dish of about 6 inches in diameter, and allowed to evaporate spontaneously; great care was taken to avoid fluctuations of temperature which caused the deposition of small crystals unsuitable for subsequent examination, and to prevent dust from getting into the solution, as this seemed to cause the crystals to be deposited in aggregates. In properly conducted experiments, each crystal developed apart from its fellows as a right-angled prism; when the crop of crystals had grown until most were some 5 mm. or so in one direction, all were removed from the liquid, the faulty ones rejected without further examination, and the sign of the circular polarisation of each remaining crystal determined by examination in a polarising microscope under a 1-inch objective. This was done simply by rotating the analyser and noting in which direction extinction occurred; if the analyser had to be rotated to the right to give extinction, the crystal under examination was dextrorotatory, and *vice versa*. All the crystals deposited from the solution, with the exception of at most 2 or 3 per cent., which were found unsuitable owing to opacity or aggregation, were thus examined; and, in order to eliminate personal bias, we have included in our tables every observation of circular polarisation which was made, no crystal being rejected after its sign was known; this is a very necessary precaution, because we are concerned with an average result.

The results of forty-six separate crystallisations, all we have made, are stated in Table I; it will be seen that in only two cases, namely,

TABLE I.—*Deposition of Sodium Chlorate from a Pure Aqueous Solution.*

1 Number.	2 Dextro- crystals. <i>d.</i>	3 Lævo- crystals. <i>l.</i>	4 Total. <i>d + l.</i>	5 Percentage of dextro- crystals.	6 Percentage of lævo- crystals.
1	32	37	69	46·38	53·62
2	38	31	69	55·07	44·93
3	64	69	133	48·12	51·88
4	23	15	38	60·53	39·47
5	39	47	86	45·35	54·65
6	19	15	34	55·88	44·12
7	42	35	77	54·55	45·45
8	24	68	92	26·09	73·91
9	35	45	80	43·75	56·25
10	20	33	53	37·74	62·26
11	28	21	49	57·14	42·86
12	14	12	26	53·85	46·15
13	39	15	54	72·22	27·78
14	7	22	29	24·14	75·86
15	14	28	42	33·33	66·67
16	37	49	86	43·02	56·98
17	29	12	41	70·73	29·27
18	48	32	80	60·00	40·00
19	29	33	62	46·77	53·23
20	42	40	82	51·22	48·78
21	37	42	79	46·84	53·16
22	24	38	62	38·71	61·29
23	61	44	105	58·10	41·90
24	27	20	47	57·45	42·55
25	51	58	109	46·79	53·21
26	42	42	84	50·00	50·00
27	28	17	45	62·22	37·78
28	37	40	77	48·05	51·95
29	24	30	54	44·44	55·56
30	15	11	26	57·69	42·31
31	25	21	46	54·35	45·65
32	37	37	74	50·00	50·00
33	36	31	67	53·73	46·27
34	65	61	126	51·59	48·41
35	27	22	49	55·10	44·90
36	49	44	93	52·69	47·31
37	41	49	90	45·56	54·44
38	30	34	64	46·88	53·12
39	47	58	105	44·76	55·24
40	31	39	70	44·29	55·71
41	31	37	68	45·59	54·41
42	39	26	65	60·00	40·00
43	41	12	53	77·36	22·64
44	24	16	40	60·00	40·00
45	47	42	89	52·81	47·19
46	32	36	68	47·06	52·94

$$U_d = 50·83.$$

$$W_d = 50·08.$$

$$M_d = 50·08 \pm 0·11.$$

those of experiments numbered 26 and 32 respectively, were equal numbers of dextro- and lævo-rotatory crystals deposited, whilst in all other cases either more or less than 50 per cent. of the crystals obtained were dextro-rotatory. The experiments are numbered in the order in which they were performed, and in order further to eliminate personal bias, no calculations whatever were made until we considered that a sufficient number of experiments had been completed to ensure an accurate average; in fact, as little attention as possible was paid to the laboratory lists of data until the observations were concluded.

The method by which the means are calculated needs some comment. If  $d$  and  $l$  be the numbers of dextro- and lævo-rotatory crystals respectively deposited from any solution, the crop consists of  $100d/(d+l)$  per cent. of dextro-, and  $100l/(d+l)$  per cent. of lævo-rotatory individuals; these values are stated in columns 5 and 6 of Table I. An experiment, however, in which only 10 crystals are obtained is of less weight than one in which 100 crystals are obtained, the weight of an experiment being directly proportional to  $(d+l)$ . Consequently the mean value,  $U_d = \frac{100}{n} \sum \left( \frac{d}{d+l} \right)$ , where  $n$  is the number of experiments concerned, is only the unweighted mean percentage of dextro-crystals deposited. The weighted mean percentage of dextro-crystals is obviously  $W_d = \frac{100 \sum d}{\sum (d+l)}$ ; the importance of the distinction thus introduced is evident from the fact that in this series of experiments  $U_d = 50.83$  whilst  $W_d = 50.08$ . The weighted mean percentage of dextro-crystals is much more nearly 50 than is the unweighted mean.

Although the numbers given in Table I yield a weighted average result differing by only 0.08 per cent. from what was expected from theory, it is still necessary to calculate the probable mean squared error of the mean. Let the difference between the weighted mean and one individual percentage of dextro-rotatory crystals be  $\Delta = \frac{100d}{d+l} - W_d$ , then since each observation has the weight  $(d+l)$  the probable error of the weighted mean is

$$r = 0.6745 \sqrt{\frac{\sum \{(d+l)\Delta^2\}}{\{\sum (d+l) - 1\} \sum (d+l)}} = 0.11,$$

and the final value  $M_d$  for the weighted mean percentage of dextro-rotatory crystals is  $M_d = 50.08 \pm 0.11$ , and lies between 49.97 and 50.19.

We conclude, therefore, that on allowing sodium chlorate to crystallise spontaneously from pure aqueous solutions, on the average, equal numbers of the enantiomorphously related crystals are deposited.

This result is, as we have pointed out, indicated by theory and there-

fore supports the theory. But several substances which are not optically active in the amorphous state have been described by certain authors as separating from solution in unequal numbers of two enantiomorphously related crystalline forms. Thus Eakles (*Zeit. Kryst.*, 1896, 26, 562) states that on crystallising sodium periodate from aqueous solutions containing sodium nitrate, more lævo- than dextro-rotatory crystals are deposited. Further, Wyruboff (*Bull. soc. min. franç.*, 1896, 19, 219) states that he has only obtained dextro-rotatory crystals of potassium silicotungstate,  $K_4SiW_{12}O_{40} \cdot 18H_2O$ . Sodium periodate and potassium silicotungstate are, however, completely analogous to sodium chlorate in that their enantiomorphism is one of molecular, not of atomic, arrangement, and in face of the results now brought forward the above statements by Eakles and Wyruboff can hardly be accepted as conclusive until quantitative evidence is forthcoming; further, on examining Table I it will be seen that solutions of sodium chlorate sometimes yield four or five consecutive crops of crystals in which one enantiomorphous form predominates, but yet, on the average, equal numbers of crystals of each hand are obtained. Some phenomenon such as this may have led to the results obtained by Eakles and by Wyruboff.

A solution of an optically inactive substance, such as sodium chlorate, which crystallises in an enantiomorphous system deposits on the average equal numbers of crystals of the enantiomorphously related kinds, because no directive influence is brought to bear which tends to cause selective deposition of one or other enantiomorph. The conditions might, however, be quite different if in the crystallising sodium chlorate solution there were dissolved an enantiomorphous substance containing an asymmetric carbon atom such as dextroglucose; it could not be stated on *à priori* grounds that there would be the same tendency for dextro- as for lævo-sodium chlorate to crystallise from a solution containing dextroglucose, and dextro- and lævo-sodium chlorates might have different solubilities in a dextroglucose solution. Although as an abstract principle the above statement appears sound, yet no opinion can be formed as to how great the directive tendency of the dissolved optically active substance would be, and it might well be so slight as to be practically inappreciable. No experiments bearing on this question are on record, and we have therefore examined the way in which several carbohydrates containing asymmetric carbon atoms affect the crystallisation of sodium chlorate, the result being that positive evidence of an influence exerted by the optically active substance in solution has been obtained.



*Deposition of Sodium Chlorate from a Dextrose Solution.*

A quantity of a nearly saturated aqueous solution of sodium chlorate was gently warmed with dextroglucose until the latter was wholly dissolved; the colourless solution which then contained 200 grams of dextrose per litre was filtered and placed in crystallising dishes of about 6 in. diameter. The liquid thus obtained showed no evidence of chemical change

TABLE II.—*Crystals of Sodium Chlorate deposited from a Solution containing 200 grams of Dextrose per Litre.*

Number.	Dextro-crystals. <i>d.</i>	Lævo-crystals. <i>l.</i>	Total. <i>d+l.</i>	Percentage of dextro-crystals.	Percentage of lævo-crystals.
1	32	71	103	31·07	68·93
2	47	89	136	34·56	65·44
3	44	107	151	29·14	70·86
4	24	51	75	32·00	68·00
5	37	70	107	34·58	65·42
6	19	27	46	41·30	58·70
7	39	91	130	30·00	70·00
8	42	46	88	47·73	52·27
9	28	64	92	30·43	69·57
10	31	66	97	31·96	68·04
11	29	79	108	26·85	73·15
12	36	104	140	25·71	74·29
13	17	38	55	30·91	69·09
14	42	96	138	30·43	69·57
15	9	21	30	30·00	70·00
16	25	63	88	28·41	71·59
17	39	84	123	31·71	68·29
18	21	43	64	32·81	67·19
19	26	61	87	29·89	70·11
20	30	79	109	27·52	72·48
21	37	65	102	36·27	63·73
22	23	51	74	31·08	68·92
23	40	76	116	34·48	65·52
24	49	113	162	30·25	69·75
25	15	24	39	38·46	61·54

$$U_d = 32·30.$$

$$W_d = 31·75.$$

having occurred, and on cooling deposited no crystals; on allowing the rather syrupy solution to evaporate spontaneously in the air at constant temperature and in as complete absence of dust as possible, large, well-developed crystals of sodium chlorate began to separate after a week or so. These crystals were separated as before, being sorted into dextro- and lævo-crystals; the results are given in Table II. After examination, the crystals were dissolved in the minimum quantity of hot water, the solution mixed with the mother liquor, and, after filtra-

tion, the liquid was again put to crystallise. The same precautions to avoid personal bias were taken as in the preceding case.

The results quoted in this table show distinctly that an optically active enantiomorphous substance dissolved in a solution of a purely crystallographically enantiomorphous compound materially affects the proportion in which the enantiomorphously related crystals are deposited. More than twice as many lævo- as dextro-rotatory crystals of sodium chlorate are deposited from a sodium chlorate solution containing 20 per cent. of dextrose. It is further not easy to realise that this directive influence could be attributed to chemical action; the crystals deposited consist of sodium chlorate and the preponderance of the lævo-rotatory crystals apparently has a purely physical cause.

*Deposition of Sodium Chlorate from Mannitol Solution.*

It has been noted above that circular polarisation is only one mode of expression of enantiomorphism. It would not be expected, therefore, that the magnitude of the specific rotation of a dissolved substance should be directly connected with the influence which the latter substance exerts on the proportion in which enantiomorphously related crystals are deposited. The related factor is the enantiomorphism, which, in the case of dextrose, is an enantiomorphism of atomic arrangement, and in that of the sodium chlorate an enantiomorphism of molecular arrangement. In order to test the truth of this view, experiments were made with mannitol, which, although an enantiomorphous substance, is practically inactive in aqueous solution; Müntz and Aubin (*Ann. chim. phys.*, [v], 10, 533) found it to be inactive in

TABLE III.—*Crystals of Sodium Chlorate deposited from a Solution containing 50 grams of Mannitol per Litre.*

Number.	Dextro-crystals. <i>d.</i>	Lævo-crystals. <i>l.</i>	Total. <i>d + l.</i>	Percentage of dextro-crystals.	Percentage of lævo-crystals.
1	7	9	16	43·75	56·25
2	5	6	11	45·45	54·55
3	6	7	13	46·15	53·85
4	7	5	12	58·33	41·67
5	37	64	101	36·63	63·37
6	1	1	2	50·00	50·00
7	1	2	3	33·33	66·67
8	34	11	45	75·56	24·44
9	4	15	19	21·05	78·95
10	8	13	21	38·10	61·90
11	8	10	18	44·44	55·56

$$U_d = 44·80,$$

$$W_d = 44·83,$$

aqueous solution, and Bouchardat (*Compt. rend.*, 80, 120) assigns to it the specific rotation  $[\alpha]_D = -0.25^\circ$ , whilst dextroglucose has a high specific rotatory power greater than  $[\alpha]_D = 50^\circ$ .

Owing to the sparing solubility of mannitol, less of this carbohydrate was dissolved than in the case of dextrose. Each litre of saturated sodium chlorate solution had dissolved in it 50 grams of carefully purified mannitol; the solution was put to crystallise, and the crystals were examined as before, with the sole exception that we did not take

TABLE IV.—*Crystals of Sodium Chlorate deposited from a Solution containing 60 grams of Mannitol per Litre.*

Number.	Dextro-crystals. <i>d.</i>	Laevo-crystals. <i>l.</i>	Total. <i>d+l.</i>	Percentage of dextro-crystals.	Percentage of laevo-crystals.
1	5	6	11	45.45	54.55
2	4	13	17	23.53	76.47
3	3	10	13	23.08	76.92
4	10	9	19	52.63	47.37
5	4	6	10	40.00	60.00
6	3	4	7	42.86	57.14
7	7	9	16	43.75	56.25
8	9	8	17	52.94	47.06
9	7	11	18	38.89	61.11
10	6	13	19	31.58	68.42
11	11	24	35	31.43	68.57
12	21	36	57	36.84	63.16
13	13	16	29	44.83	55.17
14	19	18	37	51.35	48.65
15	14	20	34	41.18	58.82
16	11	19	30	36.67	63.33
17	27	36	63	42.86	57.14
18	17	28	45	37.78	62.22
19	19	41	60	31.66	68.34
20	21	16	37	56.76	43.24
21	7	12	19	36.84	63.16
22	39	57	96	40.63	59.37
23	22	34	56	39.29	60.71
24	36	59	95	37.89	62.11
25	27	14	41	65.85	34.15
26	19	29	48	39.58	60.42
27	11	26	37	29.73	70.27
28	31	48	79	39.24	60.76
29	7	11	18	38.89	61.11
30	3	9	12	25.00	75.00
31	14	10	24	58.33	41.67
32	39	62	101	38.61	61.39
33	24	37	61	39.34	60.66
34	12	20	32	37.50	62.50
35	14	15	29	48.28	51.72
36	10	17	27	37.04	62.96
37	16	21	37	43.24	56.76

$$U_d = 40.58.$$

$$W_d = 40.55.$$

any special precautions to keep the liquid dust-free. The results are summarised in Table III.

The results show that, whilst the weight of the mannitol used was only one-fourth of the weight of dextroglucose used in the previous experiments, the deviation from equal proportions of dextro- and lævo-sodium chlorate deposited is about one-third as great with the mannitol as with the dextrose solutions. Weight for weight, then, in spite of its scarcely perceptible rotatory power in aqueous solution, mannitol would seem to exert at least as great a directive influence as dextrose in experiments of this kind.

Another series of experiments was made with a slightly stronger solution of mannitol, namely, one containing 60 grams of mannitol per litre of saturated sodium chlorate solution, and the results tabulated in Table IV will be seen to show a greater diminution in the number of dextro-sodium chlorate crystals deposited; care was taken in this case to keep the solutions dust-free and at uniform temperature. We do not lay much stress upon the percentage of carbohydrate present in the solution, as although we know the amount put into the solution, we do not know exactly what proportion was present during crystallisation after a certain amount of water had necessarily evaporated.

Although mannitol is nearly inactive in aqueous solution, yet it was just possible that the sodium chlorate might exert an influence similar to that of boric acid and increase the specific rotatory power very considerably. In order to gain information on this point, quantities of 2, 3, 4, and 6 grams of mannitol were dissolved and made up to 100 c.c. with saturated sodium chlorate solution, and examined polarimetrically; in no case could rotation be observed in 400 mm. tubes, showing that the rotation was less than 3 or 4 minutes. The specific rotatory power of mannitol in saturated sodium chlorate solution is thus of the same order as in aqueous solution; this may perhaps be considered as corroborative evidence of the absence of chemical action between the sodium chlorate and the carbohydrate.

#### *Crystals of Sodium Chlorate deposited from Isodulcitol Solution.*

A few experiments made with a saturated solution of sodium chlorate containing 50 grams of isodulcitol per litre indicated that such solutions deposit a greater number of crystals of dextro- than of lævo-sodium chlorate. The quantity of isodulcitol at our disposal was, however, small, and as we had already obtained ample experimental evidence that optically active substances in solution do exert a directive or enantiomorphous influence on the kind of crystal deposited, the experiments were not carried out in detail.

*Crystals of Sodium Chlorate deposited from Solutions containing Dulcitol.*

Until recently there has been some doubt as to whether dulcitol is, or is not, an enantiomorphous substance, but the work of Crossley (*Ber.*, 1892, 25, 2564) and others has definitely shown that this carbohydrate is not enantiomorphous. It seemed of interest, however, to determine the proportion in which dextro- and lævo-sodium chlorate

TABLE V.—*Crystals of Sodium Chlorate deposited from Solutions containing 20 grams of Dulcitol per Litre.*

Number.	Dextro-crystals. <i>d.</i>	Lævo-crystals. <i>l.</i>	Total. <i>d+l.</i>	Percentage of dextro-crystals.	Percentage of lævo-crystals.
1	36	44	80	45.00	55.00
2	54	58	112	48.21	51.79
3	27	19	46	58.70	41.30
4	26	31	57	45.61	54.39
5	46	25	71	64.79	35.21
6	26	25	51	50.98	49.02
7	17	23	40	42.50	57.50
8	32	41	73	43.84	56.16
9	36	41	77	46.75	53.25
10	19	24	43	44.19	55.81
11	42	33	75	56.00	44.00
12	21	21	42	50.00	50.00
13	34	27	61	55.74	44.26
14	26	18	44	59.09	40.91
15	34	26	60	56.67	43.33
16	29	24	53	54.72	45.28

$$U_d = 51.42.$$

$$W_d = 51.27.$$

separate from solutions containing dulcitol, but owing to the sparing solubility of dulcitol in water or sodium chlorate solution, little positive evidence could be obtained. The saturated sodium chlorate solution contained 20 grams of dulcitol per litre, and the results, which are given in Table V, show that nearly equal numbers of dextro- and lævo-sodium chlorate crystals are deposited. It ought to be observed that we should not be justified in drawing the conclusion that a substance is not enantiomorphous from experiments of the kind described in the present paper; we could, however, conclude with certainty that a compound was enantiomorphous if the value of  $W_d$  differed considerably from 50.

The results described in the preceding pages are summarised in Table VI, and allow of the deduction of the following conclusions.

1. On crystallising a substance which is not enantiomorphous in the



TABLE VI.—*Comparison of Results.*

Solution.	Number of		$U_d$ .	$W_d$ .
	Experi- ments.	Crystals.		
Pure $\text{NaClO}_3$ solution .....	46	3137	50·83	50·08
$\text{NaClO}_3$ sol. +20 per cent. dextrose .....	25	2460	32·30	31·75
„ +5 „ mannitol.....	11	261	44·80	44·83
„ +6 „ .....	37	1386	40·58	40·55
„ +2 „ dulcitol .....	16	985	51·42	51·27

amorphous state, but is enantiomorphous in the crystalline state, under conditions such that no enantiomorphous influence is brought to bear, equal numbers of the enantiomorphously related crystals are on the average deposited.

2. On crystallising a substance which is not enantiomorphous in the amorphous state, but is enantiomorphous in the crystalline state, the average ratio of the numbers in which the enantiomorphously related crystals are deposited may be made to differ from unity by introducing into the crystallising solution a substance which is enantiomorphous in the amorphous state.

3. The results obtained by crystallising sodium chlorate from solutions containing mannitol indicate that the deflection of the ratio of dextro- to lævo-crystals of sodium chlorate deposited is not directly dependent on the specific rotatory power of the dissolved substance; in doubtful cases, it might be possible to prove that a substance is enantiomorphous in the amorphous state by examining crystals of sodium chlorate deposited from its aqueous solution.

4. The enantiomorphism of a chemical nature of one substance may influence the enantiomorphism of a purely physical or crystallographic nature of another substance.

Attention should be drawn to the analogy between the results now recorded and those which we have recently obtained by crystallising sodium ammonium dextro- and lævo-tartrates from solutions containing dextroglucose (Proc., 1898, 113). On crystallising an externally compensated mixture of the two tartrates from an aqueous solution containing dextrose, the first crop contains a large excess of sodium ammonium dextrotartrate; the dextrotartrate thus appears to be less soluble than its lævo-isomeride in dextrose solution, just as lævo-sodium chlorate seems to be less soluble than its dextro-isomeride in dextrose solution. Further experiments respecting these points are in progress.

LXIV.—*Solubility of Isomeric Substances.*

By JAMES WALKER and JOHN K. WOOD.

CARNELLEY and THOMSON (Trans., 1888, 53, 782), from an extensive investigation of published data, and from experiments made in this laboratory, formulated the following rules concerning the solubility of isomerides.

1. For a group of isomeric organic substances, the order of solubility is also the order of the melting points, the most soluble isomeride being the most easily fusible.

2. The order of solubility is always the same, independent of the solvent employed.

3. The ratio of the solubilities of two isomerides is nearly independent of the nature of the solvent.

As experimental data were wanting for the establishment of the last rule, they performed a series of experiments on the solubility of para- and meta-nitraniline in various solvents, and found that the ratio of the solubility of the meta- to the para-compound varied between 1.15 and 1.48; or, if we exclude water and methylic alcohol, for which these extreme values were obtained, the variation for 11 solvents is only between 1.21 and 1.35. The authors announced their intention to extend their investigation to other substances, and also to ascertain the effect of temperature on the ratio, if any; but the death of Professor Carnelley prevented the execution of this project. With Dr. Thomson's consent, we have undertaken a continuation of the research, and now publish the results we have arrived at.

It is well known that salicylic acid and parahydroxybenzoic acid can be easily separated by means of chloroform, but if rule 3 were even approximately true, it is evidently a matter of indifference, so far as the success of the separation is concerned, what solvent is used. We therefore suspected that this case would prove an exception to the rule, and subjected the solubility of the three isomeric hydroxybenzoic acids to an investigation with water, acetone, ether, and benzene as solvents, temperature experiments being performed with water and benzene. These solvents were chosen on account of the very different associative power they exercise on substances dissolved in them; in benzene, the associative power is greatest; in water, it is non-existent, being replaced, rather, by a dissociative power in the case of acids; acetone and ether are intermediate.

*Acidimetry of Salicylic Acid and its Isomerides.*

As the solutions of salicylic acid in water at low temperatures are necessarily very dilute, it was of importance to find an indicator which would indicate sharply the point of neutralisation by a dilute solution of an alkali. Phenolphthalein, which is the usual indicator employed for salicylic acid, we found to be extremely unsatisfactory, the end-point being indefinite. Methyl-orange, litmus, lacmoid, and other acidic indicators are likewise unsuited to the purpose, but we found that Congo-red yielded excellent results; this indicator changes colour sharply when the carboxyl group is neutralised, and remains quite unaffected by the presence of the phenolic hydroxyl group. A solution of baryta, which was the alkali we always used, standardised with pure succinic acid (phenolphthalein being the indicator), was found to contain 0.001370 gram of baryta per cubic centimetre; standardised against a weighed quantity of salicylic acid, with Congo-red as indicator, it apparently contained 0.001368 gram per c.c. Again, a weighed quantity of salicylic acid was dissolved in water, and titrated with a known baryta solution; the quantity of salicylic acid estimated in this way was 0.1644 gram, the quantity taken being 0.1642 gram. A similar experiment with parahydroxybenzoic acid gave 0.1659 gram instead of 0.1660 gram.

It was ascertained that solutions of the acids in ether or acetone could be titrated directly with baryta and Congo-red, after previously diluting with water. In the case of benzene, the solvent had to be driven off by evaporation before the titration could be performed; if the evaporation was carried out at the ordinary pressure, part of the salicylic acid was lost as vapour, but under diminished pressure no loss took place; thus 0.0221 gram dissolved in 50 c.c. of benzene, evaporated under diminished pressure, dissolved in water, and titrated, gave 0.0223 gram.

*Solubility of Salicylic Acid.*

In every case we arrived at the saturation point of the solution from opposite directions; an unsaturated and a supersaturated solution were kept in presence of the solid substance, in a bath of constant temperature, until after filtration both solutions showed the same concentration. The solutions were usually agitated by means of stirrers driven by a small turbine, but at the higher temperatures this was sometimes found to be unnecessary, equilibrium being reached very rapidly with only occasional agitation by hand. The filtration took place by suction, within the solution itself, while it was still in the bath of constant temperature.

Our results are given in the following table, the solubilities being expressed in grams per hundred grams of solvent.

Temperature.	Solubility.	Temperature.	Solubility.
12.1°	0.1395	48.6°	0.511
23.0	0.204	56.0	0.688
28.1	0.247	64.0	0.996
34.4	0.305	66.0	1.17
38.7	0.359	75.0	1.76

The values obtained for the solubility of salicylic acid by previous observers are surprisingly divergent. Bourgoin (*Bull. Soc. Chim.*, [ii], 31, 57) made a series of determinations from 0° to 75°, with every appearance of accuracy, yet his results differ altogether from those of Alexéeff, Kolbe, Ost, and others. For example, Alexéeff finds at 12.5° the solubility 0.16, while Bourgoin finds 0.206 at the same temperature. At 66°, Alexéeff finds 1.27, and Bourgoin 1.63. Kolbe and Lantemann find 0.092, and Ost 0.091 to 0.093 for the solubility at 0°; Bourgoin finds 0.15. Thus Bourgoin's results are sometimes 50 per cent. above those of other investigators. Our own numbers are considerably under Bourgoin's; indeed, if we increase ours by half their value, we obtain numbers which are very nearly identical with the values obtained by Bourgoin. This is exhibited in the following table, where the values for corresponding temperatures are compared.

	10°.	20°.	30°.	40°.	50°.	60°.	70°.
W. and W.....	0.129	0.184	0.264	0.377	0.540	0.820	1.32
W. and W. × 1.5...	0.193	0.276	0.396	0.565	0.810	1.230	1.98
Bourgoin .....	0.190	0.270	0.390	0.555	0.800	1.225	1.99

We are not in a position to explain this great and constant percentage difference between Bourgoin's results and our own; we have checked our method and numbers repeatedly, and have always arrived at sensibly the same figures. An examination of Bourgoin's paper shows no source of error, but in consideration of the fact that his values for the solubility differ, not only from ours, but from those of all other observers, we are forced to conclude that his numbers are affected by some error in a constant ratio. The only probable assumption to make is, that he did not work with pure salicylic acid at all, although he states that the acid he employed was a very pure synthetic acid; the solubilities of the other isomerides are greater than the solubility of salicylic acid, and the para-acid was a likely impurity in a salicylic acid prepared synthetically twenty years ago. If, therefore, Bourgoin's acid contained parahydroxybenzoic acid as an impurity, it would give numbers for the solubility in excess of those obtained for pure salicylic acid; the excess of 50 per cent. is, however, almost too great and too constant

to be explicable in this way. In order to make certain that the salicylic acid we ourselves employed was pure, we recrystallised a quantity successively from water and from benzene, and found that the solubility and the melting point remained unchanged.

To express the variation of the solubility of salicylic acid with temperature, Bourgoin gives the following formula for the range between  $0^{\circ}$  and  $35^{\circ}$ .

$$S = 0.0002 (t^2 + 10t + 750).$$

Two-thirds of the values of  $S$  obtained from this equation will express our numbers with fair accuracy. We find, however, that a formula of the type proposed by Nordenskjöld is quite as accurate and equally simple, while it extends over a larger range of temperature. It has the form

$$\text{Log } S = 0.01556t - 1.0458,$$

and holds good between  $0^{\circ}$  and  $56^{\circ}$ . The calculated and observed values are given below.

	$0^{\circ}$	$12.1^{\circ}$	$23.0^{\circ}$	$28.1^{\circ}$	$34.4^{\circ}$	$38.7^{\circ}$	$48.6^{\circ}$	$56^{\circ}$
Obs.	0.092	0.139	0.204	0.247	0.305	0.359	0.511	0.688
Calc.	0.090	0.139	0.205	0.246	0.309	0.360	0.513	0.669

Above  $60^{\circ}$ , the formula is no longer valid.

The values obtained for the solubility of salicylic acid in benzene are given below, the solubility being again expressed in parts of salicylic acid dissolved by 100 parts by weight of the solvent.

$t$	$11.7^{\circ}$	$18.2^{\circ}$	$30.5^{\circ}$	$34.6^{\circ}$	$36.6^{\circ}$	$49.4^{\circ}$	$64.2^{\circ}$
$S$	0.460	0.579	0.991	1.261	1.430	2.380	4.40

In this case, the solubility cannot be expressed by a formula of the simple Nordenskjöld type. What here holds good of salicylic acid also holds good of its isomerides; in each case, the variation of the solubility in water with the temperature can be expressed by a simple logarithmic formula, whilst the variation of the solubility in benzene cannot be so expressed.

Determinations of the solubility of the acid in acetone and in ether gave the following results. 100 c.c. of the acetone solution at  $23^{\circ}$  contained 31.3 grams of the acid; and 100 c.c. of the ethereal solution at  $17^{\circ}$  contained 23.4 grams.

#### *Solubility of Metahydroxybenzoic Acid.*

The following table gives the number of grams of metahydroxybenzoic acid dissolved by 100 grams of water at different temperatures.

$t$	$13.3^{\circ}$	$18.8^{\circ}$	$24.3^{\circ}$	$30.9^{\circ}$	$36.2^{\circ}$	$51.0^{\circ}$
$S$	0.668	0.843	1.054	1.380	1.787	3.167



These results are well expressed by the logarithmic formula,

$$\text{Log } S = 0.01793t - 0.4118.$$

Extrapolating by means of this formula, we get the value 0.388 for the solubility at 0°; Ost found for this temperature 0.377; Fittica found 0.924 for 18°, our value for the same temperature being 0.815.

The solubility in benzene is much less than the solubility in water, as the following table shows, the quantities being again grams of acid in 100 grams of solvent.

<i>t</i>	25.0°	34.1°	46.0°	58.0°	64.0°
<i>S</i>	0.0101	0.0141	0.0234	0.0435	0.0592

For the solubility in acetone, we found that 100 c.c. of the solution contained 26.0 grams of acid at 23.0°; 100 c.c. of ethereal solution at 17.0° contained 9.73 grams of the acid.

#### *Solubility of Parahydroxybenzoic Acid.*

The solubility of the para-acid is intermediate between the solubilities of the ortho- and meta-compounds in the case of water, but smaller than either in the case of benzene. The results are given as before in grams of acid dissolved by 100 grams of solvent.

Water.						
<i>t</i>	12.7°	20.9°	34.4°	39.4°	46.0°	54.6°
<i>S</i>	0.307	0.492	0.987	1.211	1.815	2.740
Benzene.						
<i>t</i>	11.0°	33.0°	49.0°	64.0°	80.0°	
<i>S</i>	0.00197	0.00571	0.0155	0.0350	0.0660	

Again the solubility in water is expressible by a simple logarithmic formula, namely

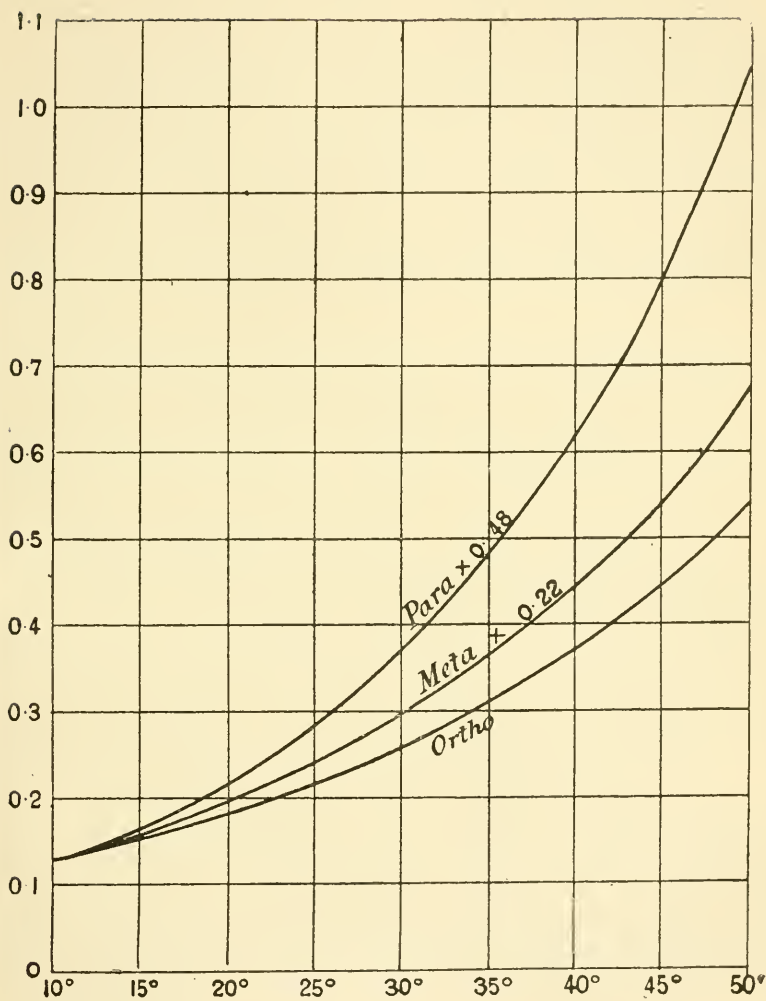
$$\text{Log } S = 0.0227t - 0.7972.$$

According to this formula, the solubility at 0° is 0.160, the value found by Ost being 0.172. Saytzeff gives the solubility at 15° as 0.793, which is far in excess of our value 0.349.

In 100 c.c. of acetone solution at 23° there are 22.7 grams of the acid, and in 100 c.c. of ethereal solution at 17° there are 9.43 grams.

#### *Comparison of Results.*

The influence of the solvent on the solubility ratios of the isomerides is apparent from the following table (p. 625). In it the solubilities are given for 30° in the case of water and benzene, 23° in the case of acetone and 17° in the case of ether.





Solvent.	Ortho.	Meta.	Para.	O/M.	O/P.	M/P.
Water...	0.264	1.337	0.765	0.197	0.345	1.75
Acetone	31.2	26.0	22.7	1.20	1.38	1.15
Ether ...	23.4	9.73	9.43	2.40	2.48	1.03
Benzene.	0.97	0.0121	0.0052	80.2	187.0	2.33

It is obvious that there is here no constancy in the ratios contained in the last three columns. The solubilities in water and in benzene are, it is true, expressed in a slightly different manner from the solubilities in acetone and in ether, but altering all the solubilities to grams in 100 c.c. of solution leaves the ratios unaffected. In water, salicylic acid is considerably less soluble than its isomerides; in the other solvents it is more soluble, especially so in benzene, which is a solvent of the same type as chloroform, the liquid usually employed to effect the separation of the synthetic salicylic acid from the isomeric acids accompanying it.

It has been held that the solubility of a solid in water is regulated, not by the total amount dissolved, but by the undissociated amount in the solution. Considering the solubility from this point of view, however, renders the difference of the O/P ratio in water and in benzene even greater than before, as the ortho-acid is more dissociated than the other, so that an explanation cannot be sought for in the theory of electrolytic dissociation.

The effect of temperature on the ratio can best be seen in the curves of the accompanying figure, p. 624, where temperatures have been plotted on the horizontal axis, and solubilities in water on the vertical axis. The curves have further been made to coincide at one temperature, namely, 10°, by multiplying the solubilities of the meta- and para-acids by 0.22 and 0.48 respectively; if the ratios of the solubilities were independent of the temperature, the curves would then coincide throughout their entire lengths, which is not in accordance with the data.

The same holds good for the effect of temperature on the solubility ratios in benzene. The reduced curves are again divergent, only in this case the ortho- and meta-curves lie much closer together, and cut each other again at about 60° if originally made to cut at 25°. The effect of temperature on the O/M ratio in benzene thus appears to be small in the range examined, but at higher temperatures the divergence of the curves would become large, and the effect on the ratio correspondingly great.

#### *Solubility of Substituted Carbamides, $C_7H_8N \cdot CO \cdot NH_2$ .*

As we did not consider that acids afforded a fair test of the general applicability of the rule of constant ratios, owing to their tendency to dissociation in aqueous solutions and to association in benzene solu-

tions, we made a series of solubility determinations of benzylcarbamide and its isomerides, in which substances both of these tendencies are small or entirely absent. The compounds we investigated were benzylcarbamide melting at  $149^{\circ}$ , unsymmetrical methylphenylcarbamide melting at  $82^{\circ}$ , orthotolylcarbamide melting at  $185^{\circ}$ , and paratolylcarbamide melting at  $173^{\circ}$ . The mode of investigation was to evaporate a measured volume of the saturated solution in a tared vessel and weigh the residue; this method gave fairly satisfactory results even with water as solvent if the evaporation were conducted on a water bath. For example, 0.0447 gram of benzylcarbamide, when dissolved in water and the solution evaporated to dryness, lost only 0.0001 gram. The only case where the loss under our experimental conditions is considerable is with the aqueous solution methylphenylcarbamide, which requires prolonged heating at  $100^{\circ}$  to effect the complete removal of the water; direct experiment showed that here a correction of 5 per cent. has to be applied in order that the solubility may be judged by the weight obtained on evaporation of the aqueous solution.

Our results are exhibited in the accompanying table, the solubilities being everywhere expressed in grams of dissolved substance in 100 c.c. of solution. The numbers were obtained at  $45^{\circ}$  for water,  $44.2^{\circ}$  for benzene,  $23^{\circ}$  for acetone, and  $22.5^{\circ}$  for ether.

	Methyl-phenyl M.	Benzyl B.	Paratolyl P.	Orthotolyl O.
Water.....	74.0	1.71	0.307	0.251
Acetone .....	29.4	3.10	2.66	0.462
Ether .....	2.28	0.053	0.062	0.0162
Benzene .....	12.48	0.0597	0.043	0.0155

The ratios of these numbers are again far from constant, as the following table shows.

	M/B.	M/P.	M/O.	B/P.	B/O.	P/O.
Water.....	43.3	241	295	5.57	6.81	1.22
Acetone .....	9.48	11	63.6	1.17	6.71	5.76
Ether .....	43.0	36.8	141	0.85	3.27	3.82
Benzene .....	209.0	290	805	1.39	3.85	2.77

### *Conclusions.*

The rule that the order of fusibility of isomeric substances is also the order of their solubility does not hold good for the hydroxybenzoic acids, as may be seen from the following table.



*Solubility.*

Fusibility.	Water.	Acetone.	Ether.	Benzene.
O	O	P	P	P
M	P	M	M	M
P	M	O	O	O

The rule is in general applicable to benzylcarbamide and its isomerides, the only exception found being benzyl- and paratolyl-carbamide in ether, where the solubilities lie close together, but not in the order of fusibility.

The rule that the order of solubility is independent of the solvent is subject to the same exceptions as the preceding rule.

The constancy of the solubility ratio observed by Carnelley and Thomson for meta- and para-nitraniline is not found either with the hydroxybenzoic acids or with benzylcarbamide and its isomerides. The solubility ratio for any pair of the hydroxybenzoic acids in the same solvent is also variable with the temperature.

The variation of the solubility of salicylic acid and its isomerides with the temperature can be expressed by a formula of the type proposed by Nordenskjöld, namely,  $\log S = aT - b$ , when the solvent is water, but not when the solvent is benzene.

Congo-red was found to be the best acidimetric indicator for salicylic acid and its isomerides. The values obtained for the solubility of salicylic acid in water are only two-thirds of the values given by Bourgoin.

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## LXV.—*Constitution of Oleic Acid and its Derivatives.* *Part I.*

By FRANK GEORGE EDMED, B.Sc., A.R.C.S.

It was found by Saytzeff (*J. Russ. Chem. Soc.*, 1885, 417) that the product of the oxidation of oleic acid by weak alkaline permanganate was a dihydroxystearic acid,  $C_{18}H_{36}O_4$ , melting at  $134^\circ$ , and that elaidic acid, on similar treatment, yielded an acid of the same composition but melting at  $99^\circ$ . Apparently, however, he did not investigate the further action of the permanganate in order to discover what were the final products of the oxidation.

These experiments were therefore repeated, and it was found that whilst these dihydroxystearic acids are undoubtedly the chief products

of the reaction, yet if the action of the permanganate be prolonged, or if the solution be heated, there are produced from both oleic and elaidic acids three other acids, namely, pelargonic acid,  $C_9H_{18}O_2$ , azelaic acid,  $C_9H_{16}O_4$ , and oxalic acid, and these seem to be the sole products.

The question then arose whether these products were the result of the direct oxidation of the oleic and elaidic acids, or were formed by the action of the permanganate on the dihydroxystearic acids; accordingly, the latter acids were subjected to the action of alkaline permanganate and were found to yield the same products, namely, pelargonic, azelaic, and oxalic acids. No evidence whatever of the formation of sebaic, suberic, or caprylic acids could be obtained, although these acids are usually stated to be the oxidation products of dihydroxystearic acid (Spiridonoff, *J. Russ. Chem. Soc.*, 1887, 646).

These results indicate that the first action of the permanganate consists in the addition of two hydroxyl groups to the unsaturated acid, forming a compound to which the following formula must be ascribed,  $CH_3 \cdot [CH_2]_7 \cdot CH(OH) \cdot CH(OH) \cdot [CH_2]_7 \cdot COOH$ , and under favourable conditions the yield appears to be quantitative. By the continued action of the permanganate, this intermediate product is destroyed, the chain breaking between the pair of carbon atoms which carry the hydroxyl groups, thus giving rise to pelargonic and azelaic acids,  $CH_3 \cdot [CH_2]_7 \cdot COOH$  and  $COOH \cdot [CH_2]_7 \cdot COOH$ , whilst oxalic acid is produced at the same time, probably from the oxidation of the chain of carbon atoms which would otherwise give rise to pelargonic acid.

The formation of these two acids appears to afford conclusive evidence in favour of the formula  $CH_3 \cdot [CH_2]_7 \cdot CH : CH \cdot [CH_2]_7 \cdot COOH$ , for both oleic and elaidic acids (compare Baruch, *Ber.*, 1894, 27, 172), since it is difficult to account for the formation of pelargonic and azelaic acids on any other assumption. The quantity of pelargonic acid formed is generally much less than that of the azelaic acid, and it would seem as if that portion of the molecule which on breaking down gives rise to pelargonic acid undergoes further oxidation, or it may be that, since pelargonic acid is soluble to a moderate extent in water and is not very volatile with steam, it is imperfectly separated from the other products of the action.

#### *Oxidation by means of Permanganate in an Alkaline Solution.*

I. \* *Oleic acid* melting at  $13-15^\circ$ .—Fifty grams of oleic acid were dissolved in 40 grams of potassium hydroxide contained in 1 litre of

\* The oleic acid was obtained from Kahlbaum, and after recrystallisation from alcohol was perfectly colourless.

water, and 120 grams of potassium permanganate in 5 litres of water, were added slowly with constant stirring. No perceptible rise of temperature occurred, and when all had been added steam was blown in until the temperature rose to  $60^{\circ}$ , and the green manganate at first formed was completely reduced; the precipitated oxides of manganese were then filtered off, and the solution acidified with dilute sulphuric acid. The dihydroxystearic acid which was precipitated was collected, and after two crystallisations from alcohol melted at  $134^{\circ}$ . It is easily soluble in hot, but much less so in cold alcohol, and it forms a characteristic calcium salt,  $\text{Ca}(\text{C}_{18}\text{H}_{34}\text{O}_4)_2 + 3\text{H}_2\text{O}$ .

The filtrate from this acid was steam distilled, when a colourless oil passed over of a peculiar odour and soluble in water; the distillate was rendered alkaline with sodium carbonate, evaporated to dryness, and acidified, when a small quantity of a colourless oil separated, having the odour of pelargonic acid. The quantity was insufficient for analysis; the same oil, however, was obtained in larger quantity from elaidic acid where the existence of pelargonic acid was definitely settled by analysis.

When the residue of the distillation was evaporated to a small bulk, an acid crystallised out, which was collected, dried, and recrystallised from hot water; it melted at  $105\text{--}107^{\circ}$  (melting point of azelaic acid,  $106^{\circ}$ ). The acid obtained was dissolved in ammonia, calcium chloride added, and the calcium salt collected, dried, and the percentage of calcium determined by heating with sulphuric acid.

Found Ca .....	17.54 per cent.
Theory Ca in $\text{Ca}(\text{C}_9\text{H}_{14}\text{O}_4)$ .....	17.70 ,,

It was thus proved to be azelaic acid. The remainder of the solution reduced permanganate with much effervescence on gently warming. Ammonia was added until alkaline, then calcium sulphate, and the precipitated calcium salt, after being boiled with acetic acid, was collected, washed, dried, and ignited. As it gave off carbon monoxide and did not blacken, it was assumed to be calcium oxalate.

II. *Elaidic acid* melting at  $45^{\circ}$ .—Fifteen grams of elaidic acid were treated with 20 grams of potassium hydroxide in  $\frac{1}{2}$  litre of water and 37 grams of permanganate in  $1\frac{1}{2}$  litres of water, the method of procedure being exactly as previously described.

The dihydroxystearic acid obtained was more soluble in alcohol than the preceding one, and after recrystallisation melted at  $99^{\circ}$ . The filtrate, on steam distilling, gave an oil similar to that obtained above but in larger quantity; it was separated from the distillate, treated with zinc oxide and water, and well boiled. The zinc salt of the acid thus obtained, on recrystallisation from alcohol, melted at  $129\text{--}130^{\circ}$  (m. p. for zinc pelargonate,  $131^{\circ}$ ).

On analysis.

Found Zn .....	17·17 per cent.
Theory Zn in $(\text{CH}_3 \cdot [\text{CH}_2]_7 \cdot \text{COO})_2\text{Zn} \dots$	17·15 „

The azelaic acid was removed and recrystallised, and the presence of oxalic acid confirmed as before.

III. *Dihydroxystearic acid* melting at  $134^\circ$ .—Forty grams of dihydroxystearic acid (prepared from oleic acid as above) were treated with 10 grams of potassium hydroxide in 1 litre of water and 55 grams of potassium permanganate in 3 litres of water added, the solution being heated nearly to boiling during the addition of the permanganate. The oxides of manganese were filtered off, and the solution acidified with dilute sulphuric acid, when a solid, colourless acid was precipitated; on heating the solution, however, this nearly all dissolved, leaving only a small quantity of solid, insoluble matter. The whole was then steam distilled, when an oil passed over with the steam which in odour, colour, and solubility resembled the pelargonic acid obtained above; this was removed and treated with zinc oxide, the zinc salt crystallised from alcohol and its melting point determined; it melted at  $129^\circ$  and was therefore zinc pelargonate.

The undissolved residue was filtered off when hot, washed until free from sulphuric acid, and dissolved in ammonia; calcium chloride was then added, and the calcium salt dried and analysed.

Found Ca .....	5·00 per cent.
Theory Ca in $\text{Ca}(\text{C}_{18}\text{H}_{34}\text{O}_4)_2 + 3\text{H}_2\text{O}$	5·46 „

This showed that the insoluble portion was merely unchanged dihydroxystearic acid. On evaporating the rest of the solution, azelaic acid crystallised out and was identified by its melting point ( $106^\circ$ ). The remainder of the solution was treated with calcium sulphate, the precipitate boiled with acetic acid, and oxalic acid recognised in the form of its calcium salt.

IV. *Dihydroxystearic acid* melting at  $99^\circ$ .—This acid was prepared in a manner exactly similar to the preceding, but the yield was much smaller. It appears to be much more easily oxidised, hence the oxidation goes farther, with formation of correspondingly larger amounts of the final products, pelargonic and azelaic acids. This behaviour is what might be expected if we consider the stereoisomeric formulæ for oleic and elaidic acids. In this way, the formulæ for the dihydroxystearic acid melting at  $134^\circ$  would be I, whilst the other



would have the formula II. In the latter case, the close proximity of



the two hydroxyl groups to one another in the molecule would lead us to expect that it would be the more easily oxidised, and this was found to be the case.

The dihydroxystearic acid was subjected to the action of alkaline permanganate in the manner already described. On distilling the product, pelargonic acid was obtained and recognised in the form of its zinc salt, whilst from the rest of the solution azelaic and oxalic acids were obtained and identified as above described. Here also these acids appear to be the sole products of the decomposition.

*Summary of Oxidation Products.*

From oleic acid.	From claidic acid.
Dihydroxystearic acid, m. p. 134°...60 per cent.	Dihydroxystearic acid, m. p. 99°...33 per cent.
Pelargonic acid..... small	Pelargonic acid ...13—14 per cent.
Azelaic acid .....16 per cent.	Azelaic acid .....26 per cent.
Oxalic acid .....16 per cent.	Oxalic acid .....15—20 per cent.

*Oxidation of Oleic Acid with Chromic Acid.*

A 2 per cent. solution of potassium dichromate containing an equivalent quantity of sulphuric acid was added to 10 grams of oleic acid and the whole heated in a flask provided with a reflux condenser. For some time no action took place, but after about 4 days heating, reduction of the chromate began to go on very slowly; the heating was continued for 10 days, and the excess of chromate then reduced by boiling with sulphur dioxide. The solid chromic oxide was collected, boiled with dilute sodium carbonate solution, the solid filtered off, and the solution evaporated to dryness and acidified with dilute sulphuric acid; the acid thus obtained proved to be simply unchanged oleic acid. The remainder of the solution was steam distilled in order to see if any volatile acids had been formed. The distillate gave an acid reaction and had an odour resembling that of pelargonic acid, but the quantity was too small for identification by analysis. The residue in the distilling flask was extracted with ether, and a mixture of unchanged oleic acid and a colourless solid obtained; the latter was easily soluble in boiling water, and could thus be separated from the oleic acid and crystallised; it proved to be azelaic acid. No other products are formed in the reaction.

Chromic acid, therefore, seems to break up the molecule in the same manner as the permanganate. The small quantity of pelargonic acid may also be explained on the assumption that oxalic acid is formed, but that it is immediately destroyed by the powerful oxidising agent employed.



*Fusion with Potassium Hydroxide.*

As early as 1840, Varrentrap showed (*Annalen*, 1840, **35**, 195) that on fusing oleic acid with potash it was broken up into palmitic and acetic acids, and on this ground the formula for oleic acid has, until recently, been represented as containing the ethylenic linkage between the  $\alpha$ - and  $\beta$ -carbon atoms, thus,  $\text{CH}_3 \cdot [\text{CH}_2]_{14} \cdot \text{CH} : \text{CH} \cdot \text{COOH}$ .

More recent evidence tends to prove that the true formula is the symmetrical one used above, and the results of the oxidation afford additional evidence in support of this view. This being so, we should expect the fusion to give rise to pelargonic and azelaic acids. An explanation has been put forward by Wagner (*Ber.*, 1888, **21**, 3353), in which he assumes that the first action is brought about by water and atmospheric oxygen, and consists in the formation of dihydroxystearic acid,  $\text{CH}_3 \cdot [\text{CH}_2]_7 \cdot \text{CH}(\text{OH}) \cdot \text{CH}(\text{OH}) \cdot [\text{CH}_2]_7 \cdot \text{COOH}$ .

In the second stage of the reaction, the potash exerts an oxidising and a reducing action simultaneously, producing an acid of the formula  $\text{CH}_3 \cdot [\text{CH}_2]_7 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot [\text{CH}_2]_5 \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{COOH}$ . The final action is hydrolytic, palmitic acid,  $\text{C}_{15}\text{H}_{31} \cdot \text{COOH}$ , and acetic acid,  $\text{CH}_3 \cdot \text{COOH}$ , being produced.

The only other possible explanation is to assume that, under the action of the potash, the bond is caused to shift from the middle position to the end of the chain, in fact to assume that the elements of water are taken on and then eliminated in a different direction seven times in succession, just as in the case of unsaturated  $\beta\gamma$ -acids; the bond shifts under the action of alkalis to the  $\alpha\beta$ -position. The objection to this, however, is that, so far as is known, this shift of the bond is a peculiar property of  $\beta\gamma$ -acids only. No fusion of pure oleic acid with potash appears to have been described since the time of Varrentrap, and it was, therefore, deemed advisable to repeat the fusion, paying special attention to the quantitative nature of the reaction, for if any shift of the bond took place it might be expected to introduce complications which would tend to reduce the yields of the final products.

In order to minimise the chances of irregular atmospheric oxidation, the fusions were effected in an atmosphere of coal gas. Pure\* oleic and elaidic acids melting respectively at  $13^\circ$  and  $45^\circ$  were used. The acid was weighed out into a nickel crucible and the fusion carried out first at the lowest possible temperature in an oil bath, the temperature being maintained at from  $250^\circ$  to  $280^\circ$ . When the fusion was complete, the contents of the crucible were dissolved in boiling water, the solu-

\* Lant Carpenter (*J. Soc. Chem. Ind.*, 1883, p. 98) has described the fusion of oleic acid with potash, but he used crude materials only and neglected the quantitative relations of any other products save palmitic acid.

tion acidified with sulphuric acid; the solid fatty matter which separated was extracted with alcohol, the solution evaporated to dryness, and the residue weighed. The solution containing the potassium sulphate and excess of sulphuric acid was distilled, pure barium carbonate added to the distillate, which was filtered, and the filtrate evaporated to dryness in a weighed glass dish; the residue of barium acetate was then dried at  $130^{\circ}$  and weighed.

The second fusion was performed at a higher temperature, but charring was avoided.

### Results.

Oleic acid.		Wt. of palmitic acid.		Wt. of acetic acid.	
	Wt. taken.				
I.	3.97 grams	3.83 grams		0.26 gram	
		Theory 3.60	„	Theory 0.84	„
II.	3.31 „	3.28	„	0.20	„
		Theory 3.00	„	Theory 0.70	„
Elaidic acid.					
	4.54 grams	4.12 grams		0.03 gram	
		Theory 4.10	„	Theory 0.96	„

The barium salt mentioned above was found to consist only partly of barium acetate. Hence the yield of acetic acid is even less than here indicated.

Oxalic acid, the formation of which was suspected, was separated as the calcium salt, so that this acid appears to be formed, both in the case of oleic and elaidic acids, in addition to palmitic and acetic acids, although the amount does not exceed 1 per cent. of the products. Nevertheless, as will be seen, the amount of oxalic acid is greater than that of the acetic acid, since all the substance weighed as acetate was not so in reality. Palmitic acid, on the other hand, was formed in every case in practically theoretical amount.

Attempts were made to discover if any pelargonic and azelaic acids were formed in small quantities during the reaction, but none could be detected. Again, since Wagner's explanation involves the formation of dihydroxystearic acid as intermediate product, a fusion was performed using a large excess of potash, and the palmitic acid obtained was repeatedly recrystallised from alcohol, but not even in the mother liquor from the final crystallisation could any trace of dihydroxystearic acid be found. If any other products besides palmitic, acetic, and oxalic acids are formed, they are produced only in minute quantity. Finally, the action of potash on pure palmitic acid under corresponding conditions was studied, and it was found that at a temperature of from  $250^{\circ}$  to  $280^{\circ}$  practically no action occurred.

The results of these experiments show that it is unlikely that

during the fusion the bond undergoes any shift, since, if this took place, we could scarcely obtain a theoretical quantity of palmitic acid, and we should also expect to find appreciable amounts of other products, as, for example, pelargonic and azelaic acids. Hence, for the present, Wagner's explanation must be accepted, since the weight of evidence is in favour of the symmetrical formula for oleic acid, with which elaidic acid is stereoisomeric (Baruch, *loc. cit.*).

In conclusion, I wish to express my thanks to Professor Tilden, under whose valuable guidance the above experiments have been conducted.

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## LXVI.—*Reversible Zymohydrolysis.*

By ARTHUR CROFT HILL, B.A.

### INTRODUCTORY.

THIS investigation was undertaken with the object of determining if hydrolysis through the agency of enzymes is, like other chemical reactions, reversible ; if, in fact, under appropriate conditions, the corresponding synthesis can be obtained.

It was necessary to choose a very simple case of zymolytic action in which the exact stage of conversion could at any time be accurately determined, and then to ascertain if the reaction were retarded by the products formed and did not reach completion, as only such a reaction could be considered suitable for the purpose. In the case of cane-sugar and invertase, it had been found by O'Sullivan and Tompson (*Trans.*, 1890, 57, 834) that the reaction tended to total conversion, and that the time curve gave no evidence of hindering by the products of inversion ; but viewed in the light of other chemical reactions, it seemed possible that a hindering influence existed but had been small enough to escape detection. The hydrolysis of maltose differs from that of cane-sugar in that, whilst the latter is split into two dissimilar molecules, the former yields two similar molecules, and it seemed reasonable to expect that, in the hydrolysis of maltose, a hindering influence might be more marked and more easily observed. This reaction was therefore chosen, and the maltase of yeast selected as the enzyme.

Part I of this paper deals with the manner of extraction and with certain properties of the enzyme ; Part II, with the analytical methods by which the amount of change at any stages of a hydrolysis has been

estimated ; Part III is taken up with an account of experiments which show a distinct hindering action by glucose, an action which increases with the concentration of the solutions ; Part IV, with experiments showing a reverse change of glucose to maltose in concentrated solutions. It deals also with the equilibrium points, or limits of conversion, for several different concentrations.

#### PART I. EXTRACTION OF THE ENZYME.

The existence in yeast of this enzyme which converts maltose into glucose, was suspected by Bourquelot (*Journ. de l'Anatomie et de la Physiologie*, 1886, pp. 180, 200) ; he was unable, however, to get an active extract of it, using chloroform as an antiseptic. Lintner (*Zeits. d. Ges. Brauwesen*, 1892, 106), Fischer (*Ber.*, 1894, 27, 1113), Röhmann (*Ber.*, 1894, 27, 3251), and Lintner and Kröber (*Ber.*, 1895, 28, 1050) have extracted it from dry yeast. Morris (*Proc.*, 1895, 46) called attention to the fact that fresh yeast in the presence of chloroform did not attack maltose ; but it seems clear from Lintner and Kröber's (*Ber.*, 1895, 28, 1050) observations, and from observations made in the course of this research, that chloroform slowly destroys the enzyme, whilst Fischer (*Ber.*, 1895, 28, 1430) has found that fresh yeast hydrolyses maltose when, not chloroform, but thymol or toluene is used as an antiseptic.

Nevertheless, dried yeast hydrolyses much more actively than fresh yeast, for the enzyme does not leave the cells until they have been thoroughly dried. Even from dried yeast, Fischer (*Ber.*, 1894, 27, 1479) found that only a feebly active extract was obtained, so that in most of his experiments he preferred using the dried yeast itself with an antiseptic to using the extract. Lintner and Kröber's extract was more active, but they do not enter into details as to the circumstances in the preparation and extraction of the yeast which give the best results, neither do they discuss the stability of their extracts. Röhmann mentions that his yeast was heated for 1 hour at 105° to 110°, according to Barth's method, and then extracted with thymol water. He does not state how active the extract was, nor whether it kept well.

The duration of heating and the range of temperature are important ; although the enzyme is not destroyed by heating the yeast at 120° for a short time, or by heating above 105° for 6 hours, there is a decided disadvantage in such heating, for the extract filters badly, becoming distinctly more turbid when kept and losing much of its activity. The result appears to be due to rupture of the cell walls consequent on treating the highly exsiccated and damaged cells with water, whereby a most unstable proteid escapes and is gradually pre-



cipitated. A similar progressive precipitation was observed by E. Buchner (*Ber.*, 1897, 30, 117) in his expressed yeast juice. The difficulty does not occur if the heating be limited in the way which will be presently described. By using very dilute alkali for the extraction instead of distilled water, the activity of the extract is usually much increased, the effect of the alkali being to neutralise any acidity of the yeast which would prevent the enzyme from going into solution. The digesting mixture must be neutral, not alkaline, as free alkali at once destroys the enzyme.

The following method has given the best results. Good, pressed, bottom fermentation yeast\* after being pounded in a mortar with distilled water, and washed three times by decantation, is collected on a filter provided with a cover, and then spread on porous tiles and dried in a vacuum over sulphuric acid. After two days or so in the exsiccator, the yeast is dry and brittle; it is then powdered in a mortar and sifted through fine muslin, being thus obtained as a bright, yellowish-white powder. The heating is performed by suspending the powdered yeast on a double layer of fine muslin over the mouth of a glass jar, which is then placed in an oven previously heated to 40°, and the temperature is allowed to rise during successive quarters of an hour to 60°, 70°, 90°, 100°; it is then maintained at 100° for a quarter of an hour, when the jar is taken out of the bath and put in the exsiccator until cool. The yeast is weighed in a closed vessel, pounded in a mortar with ten times its weight of 0.1 per cent. sodium hydroxide solution, put into a flask, toluene added, and the whole allowed to digest at the temperature of the room for three days. The extract is then filtered, first through paper and afterwards through a Pasteur-Chamberland filter into sterilised apparatus.

As thus obtained, it is a pale yellow, clear liquid of neutral or faintly acid reaction, and yielding from 0.516 to 0.52 per cent. of ash, and from 2.45 to 3.14 per cent. of total solids. It remains bright, and has shown activity, although in diminished degree, after the lapse of some months. The test of activity is that 1 c.c. of the fresh extract acting on 20 c.c. of a 2 per cent. solution of maltose at 30°, will hydrolyse about 20 per cent. of the sugar in 40 minutes, and over 90 per cent. when left from one evening to the next morning.

If the extract, as first obtained, is feebly acid, when mixed with the sugar solution the mixture is not acid enough to react with litmus; it may be said, therefore, that the conversion proceeds in neutral solution. The addition of acid to the extract causes precipitation with loss of activity; addition of alkali, sufficient to make it alkaline to litmus, also destroys the activity. An attempt was made to see if

\* The yeast was obtained from one of the chief breweries in Bern (Aebersold's, Schauplatzgasse).



the addition of a very minute quantity of alkali or of acid would have an appreciable effect on the rate of hydrolysis. Two flasks, containing each a similar mixture of enzyme and maltose solution, and differing only in that in one sodium hydroxide had been added to the extent of 1 part in 12,000, were put in the bath at 30°, and the hydrolysis was estimated after 45 minutes; in either case, it was about 20 per cent. The contents of both flasks were neutral to litmus.

Although alcohol, as pointed out by Fischer (*Ber.*, 1894, 27, 1113) and by Röhmnn (*Ber.*, 1894, 27, 3251), so readily destroys the enzyme in the presence of water, it has no action when both it and the enzyme are dry. Some yeast powder, previously dried at 100°, was left for 3 days under alcohol dried over baryta; it was afterwards found to be quite active on maltose. A similar result was obtained with the dried and powdered extract.

Extracts prepared in the presence of chloroform were but feebly active. Further, the observation of Lintner and Kröber (*loc. cit.*), that chloroform retards the progress of the hydrolysis, has been confirmed.

## PART II. ANALYTICAL METHODS.

The methods employed for estimating the amount of hydrolysis were,

(1) Determination of the cupric-reducing power of the mixed sugars under standard conditions in terms of glucose and of maltose.

(2) Determination of the specific rotatory power. When an additional qualitative test has seemed desirable, the osazones have been prepared and separated.

For the reducing power, an adaptation from Pavy's method of estimating glucose has been found very convenient. It was selected because the conditions of titration in these experiments could be kept precisely similar throughout, whilst it requires but small quantities of sugar for the estimations, gives a large difference between the reducing powers of glucose and of maltose, with no chance of error from reoxidation, since the whole operation is completed in one flask from which the air is excluded. The larger difference in reducing powers in this method as compared with others in which simple Fehling's solution is used is accounted for, partly by increase in the copper value of glucose, and partly by a large decrease in the copper value of maltose. The composition of the Fehling's solution from which the ammoniacal solution is afterwards prepared is as under:

Solution A. 34.639 grams of recrystallised copper sulphate in 500 c.c. of water.

Solution B. 173 grams of crystallised Rochelle salt, 51.6 grams of dry sodium hydroxide, water to 500 c.c.

The ammoniacal solution is made up, as required, thus :

30 c.c. of Fehling's fluid A.

30 " " " B.

250 c.c. of solution of ammonia sp. gr. 0.922 (or 150 c.c. of sp. gr. 0.880).

Water to 500 c.c.

The titrating flask, which has a capacity of about 120 c.c., is provided with a rubber stopper with two holes, one for a tube in connection with a standard burette, the other for a tube of small diameter which carries off steam and ammonia to the sink. The tube which connects the flask to the burette is bent twice at right angles, having a horizontal part of about 15 cm., so that the burette is at a sufficient distance from the hot flask.

The method of titration is as follows : the sugar solution diluted to the proper strength being in the burette, 20 c.c. of the ammoniacal copper solution measured in a pipette and 20 c.c. of distilled water are placed in the titrating flask, and heated to boiling by a small flame. The contents of the flask are then kept just boiling by the same small flame ; at the end of 30 seconds, the amount of sugar solution supposed from a preliminary titration to be required, is run in slowly during 1 minute, and the boiling continued for 2 minutes longer, 3 minutes in all from the time the first portion of sugar solution was run in. The liquid in the flask is now either colourless, or blue, or yellow. To show the tint clearly, another flask containing distilled water is placed at the side of the first and the two viewed against a white background. If the tint is blue, in the next titration 0.1 c.c. more sugar solution is used ; if yellow, 0.1 c.c. less. The quantity taken as being correct is that which gives a colourless end-point within the required time, whilst 0.1 c.c. less gives a bluish end-point, and 0.1 c.c. more gives either a yellowish end-point or decolorises in considerably less than the 3 minutes. On all occasions, the copper solution is titrated also against a standard 0.2 per cent. solution of glucose. In very hot weather, and when a number of estimations have to be made extending over several hours, the copper solution is standardised both before and after the estimations. When fresh Fehling's solutions are made up, titrations against standard maltose solution are made in addition. The ammoniacal copper solution is made fresh, usually each day, the other solutions are kept in the dark in stoppered bottles sealed with paraffin.

The glucose and maltose used in the standard solutions and in the experiments were procured in as pure a condition as possible from Kahlbaum, Berlin, and then recrystallised, the glucose from 85 per cent. methylic alcohol, the maltose from 80 per cent. ethylic alcohol. The glucose crystals are washed by aid of the pump with methylic

alcohol, dried a short time over calcium chloride, powdered, and dried by heating first at  $60^\circ$ , and afterwards at  $110^\circ$ , until the weight is constant. The crystals of maltose containing water of crystallisation are washed with ethylic alcohol, with the aid of the pump, dried a short time over calcium chloride, powdered, and re-dried over calcium chloride for about a week. The water, the amount of which varies, is then determined in a portion of the sugar by drying it slowly up to  $110^\circ$ , and finally at  $115^\circ$ , until the weight is constant. Since maltose hydrate,  $C_{12}H_{22}O_{11} + H_2O$ , yields on hydrolysis exactly its own weight of glucose,  $C_6H_{12}O_6$ , it has been possible to simplify the calculations by always reckoning maltose in terms of the hydrate.

The standard solution of glucose is made to contain 0.2 per cent. of anhydrous glucose, and the standard solution of maltose, 0.4 per cent. of maltose hydrate. When the copper solution is just made up, it takes 4.7 c.c. of standard glucose solution or 6.2 c.c. of standard maltose solution to exactly reduce the 20 c.c. under standard conditions. The copper solution is usually allowed to stand from one to two hours before use, and the values most often then obtained are 4.65 c.c. of 0.2 per cent. glucose and 6.1 c.c. of 0.4 per cent. maltose hydrate. The reducing power of maltose hydrate, taking glucose as 100, is 38: thus,  $\frac{100 \times 4.7}{2 \times 6.2} = 37.9$  or  $\frac{100 \times 4.65}{2 \times 6.1} = 38.1$ .

In experiments I and II, it will be seen that the ratio 100 : 38.5 is used, the reason being that, in the early part of the work, the boiling was kept up for 4 minutes; it was afterwards found better to use the shorter time, by which a colourless end-point could with certainty be attained.

The reducing power of any mixture of the sugars is obtained in the same way as that of maltose, that is, by dividing the number of c.c. required of a 0.2 per cent. glucose solution by the number of c.c. required of a 0.2 per cent. solution of the mixture, when both are titrated with the same copper solution, and multiplying the quotient thus obtained by 100. To illustrate by an example; a certain mixture of the two sugars, diluted to a 0.2 per cent. concentration, gave a titration value 6.55 c.c.; the standard glucose solution gave a value 4.65 c.c. Then  $R$ , the reducing power required, is  $\frac{4.65}{6.55} \times 100 = 71$ .

Similarly, another mixture of nearly the same concentration gave, with the same copper solution, 6.75 c.c. as the titration value. Here, in the same way,  $R = 69$ . To deduce the percentage composition of the mixture from  $R$ , it is necessary to notice that a complete conversion of maltose hydrate to glucose corresponds with a change in reducing power from 38 to 100, so that a change of reducing power

from 38 to  $R$  corresponds with a partial conversion of  $\frac{R-38}{100-38}$ , or a percentage conversion of  $\frac{R-38}{100-38} \times 100$ .

Examples :—

$R = 71$  ; the conversion is  $\frac{71-38}{100-38} = 52$  per cent.

$R = 69$  ;   "       "       "       "  $\frac{69-38}{100-38} = 50$  per cent.

This relation has been tested experimentally by making trial mixtures of the two sugars in various known proportions, and then determining the percentage composition by titration. The value found agreed with the actual values to the nearest whole numbers ; for example, a mixture of equal parts of the sugars gave

$R = \frac{4.65}{6.75} \times 100 = 68.8$  ; conversion  $\frac{68.8-38}{100-38} = 49.7$  per cent. (50 per cent.). A mixture of  $\frac{3}{4}$  maltose hydrate and  $\frac{1}{4}$  glucose gave

$R = \frac{4.6}{8.6} \times 100 = 53.5$  ; conversion  $\frac{53.5-38}{100-38} = \frac{15.5}{62} = 25$  per cent.

The fact that in a mixture of two sugars the reducing power of each is unchanged, is only true, as pointed out by Kjeldahl (*Résumé du Compt. rend. des Trav. du Laboratoire de Carlsberg*, p. 11), when the total amount of copper reduced is identical with that for which the specific reducing powers have been determined, a condition complied with in these estimations.

The polarimeter used was a Landolt-Lippich half-shadow instrument made by Schmidt and Haensch ; for monochromatic light, a Landolt sodium lamp was employed, and the light filtered through a solution of potassium dichromate. A special feature of this polarimeter is that the field of view is tripartite, the two outer segments of the field changing together, and in opposite sense to the central strip, an arrangement which has been found to be very sensitive. The instrument is graduated to read to six seconds, and on a series of readings the probable error in the observed rotation is not greater than half a minute.

The optical method of estimation is, with a good instrument, sensibly more delicate than the copper method ; but the latter is a useful check on the former. Using the double method of estimation, it would be possible to calculate the percentage composition of a mixture of the sugars even if the total sugar concentration were initially unknown, whilst in the actual experiments the initial calculation of the percentage of total sugar is verified or checked by every set of estimations, and any slight destruction of sugar in the process of sterilisation is at once detected.

In experiments I and II, the copper method alone was available; in the subsequent experiments, both methods were used. A single sample removed from the experimental flask serves for the two methods. It is first diluted to a 2 per cent. concentration, with addition of sodium hydroxide to 0.2 per cent.; it is then examined polarimetrically in a 200 mm. tube of capacity about 15 c.c. Subsequently, 10 c.c. are withdrawn from the polarimeter tube, diluted to 100 c.c., and examined by the copper method.

The small quantity of enzyme solution present in the diluted samples has been found insufficient to affect either the copper determinations or the polarimetric.

### PART III. INFLUENCE OF GLUCOSE.

If during an experiment there were no destruction of enzyme, the time curve of a single hydrolysis would suffice to show whether the products of the reaction hindered it or not; for, if in that case, the glucose did not hinder, the velocity at any instant should be simply proportional to the quantity of unchanged maltose; for example, at half conversion it should be half the initial velocity.

It being, however, quite impossible to show that the enzyme escapes completely, and it being even highly probable that some slight destruction does occur, the following scheme was used for Experiments I and II. The initial velocities were compared in two flasks each containing a sugar solution of the same total concentration and with the same proportion of enzyme, the difference being that in one flask the sugar was, at the beginning of the experiment, all maltose, in the other, half maltose and half glucose. If, now, the glucose had no hindering effect, the ratio of the initial velocities to one another should not exceed 2; actually, it was much greater. Taking for the initial velocity the average velocity between the initial and first subsequent titrations, the ratio of the initial velocities in Experiment I, where the sugar concentration is 4 per cent., is about 3; in Experiment II, with a concentration of 20 per cent. it appears as 4.85. Since the ratio of the initial velocities has its maximum at the commencement of the experiment, and thenceforward diminishes, the ratio of the true initial velocities is even greater.

#### EXPERIMENT I. (See Fig. 1, p. 642.)

*Sugar concentration, 4 per cent.*

*Temperature of bath, 36°.*

Flask A.	{	2 grams of maltose hydrate.
(In bath, 3.45 p.m.).....		2 c.c. of enzyme solution.
		Water to 50 c.c.
		1 c.c. of toluene.

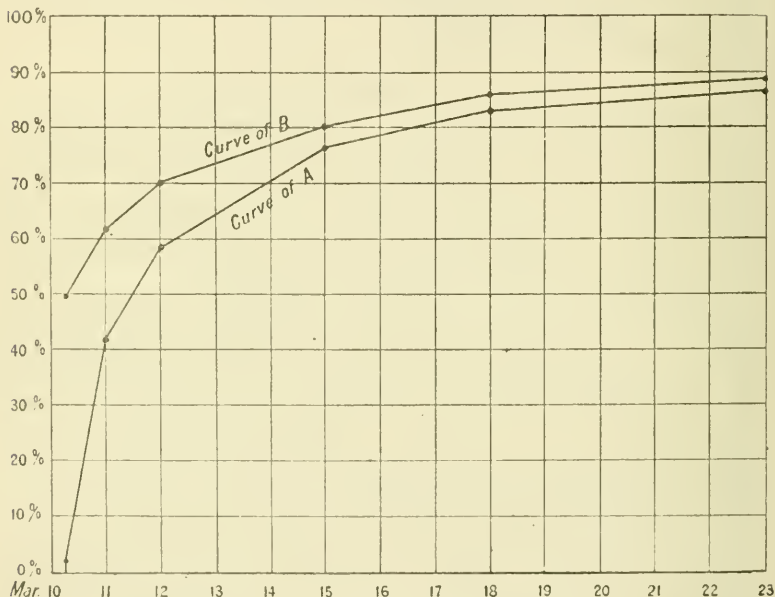


Flask B.  
(In bath, 4.30 p.m.).....

1 gram of maltose hydrate.
1 gram of glucose.
2 c.c. of enzyme solution.
Water to 50 c.c.
1 c.c. of toluene.

For titration, 5 c.c. were taken, alkalisied with 1 c.c. of 2 per cent. NaOH, and made up to 100 c.c. Time of boiling, 4 minutes. Ratio of reducing power of glucose to that of maltose, 100 : 38.5.

FIG. 1.—EXPERIMENT I.



Date.	Flask.	Titration value.	Titration of standard glucose solution.	R.	Conversion $\frac{R - 38.5}{100 - 38.5}$
March 10 (after-noon).	A	5.9 × 2	4.65	39.4	$\frac{0.9}{61.5} = 1.5$ per cent.
	B	6.75	4.65	69	$\frac{30.5}{61.5} = 49.6$ „
March 11 (morn-ing) after 18 hours.	A	7.2	4.6	64	$\frac{25.5}{61.5} = 41.5$ per cent.
	B	6.0	4.6	76	$\frac{37.5}{61.5} = 62$ „

Date.	Flask.	Titration value.	Titration of standard glucose solution.	R.	Conversion $\frac{R-38.5}{100-38.5}$
March 12 (morn- ing).	A	6.25	4.7	74.4	$\frac{35.9}{61.5} = 58.5$ per cent.
	B	5.7	4.7	81.6	$\frac{43.1}{61.5} = 70$ ,,
March 15 (morn- ing).	A	5.5	4.7	85.4	$\frac{46.9}{61.5} = 76$ per cent.
	B	5.35	4.7	87.8	$\frac{49.3}{61.5} = 80$ ,,
March 18 (morn- ing).	A	5.25	4.7	89.5	$\frac{51.0}{61.5} = 83$ per cent.
	B	5.15	4.7	91.3	$\frac{52.8}{61.5} = 86$ ,,
March 23 (morn- ing).	A	5.15	4.7	91.3	$\frac{52.8}{61.5} = 86$ per cent.
	B	5.05	4.7	93.3	$\frac{54.8}{61.5} = 89$ ,,

$$\frac{\text{Initial velocity for A} = 41.5 - 1.5}{\text{Initial velocity for B} = 62 - 49.6} = \frac{40}{13.6} = 3 \text{ (approx.)}$$

## EXPERIMENT II. (See Fig. 2, p. 644.)

*Sugar concentration, 20 per cent.*

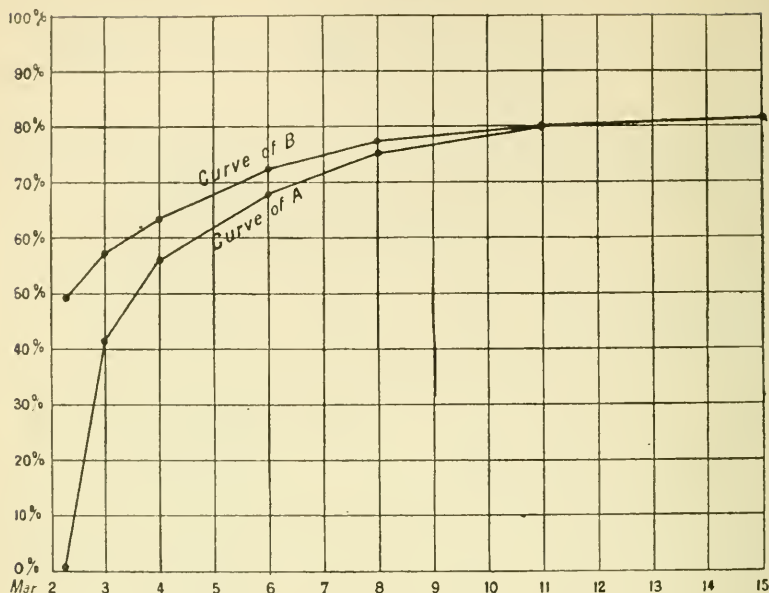
*Temperature of bath, 36°.*

Flask A.....  $\left\{ \begin{array}{l} 4 \text{ grams of maltose hydrate.} \\ 2 \text{ c.c. of enzyme solution.} \\ \text{Water to 20 c.c.} \\ \text{Toluene.} \end{array} \right.$

Flask B....  $\left\{ \begin{array}{l} 2 \text{ grams of maltose hydrate.} \\ 2 \text{ grams of glucose.} \\ 2 \text{ c.c. of enzyme solution.} \\ \text{Water to 20 c.c.} \\ \text{Toluene.} \end{array} \right.$

For titration, 1 c.c. was taken, alkalisied with 1 c.c. of 2 per cent. NaOH, and made up to 100 c.c. Time of boiling, &c., as in Experiment I.

FIG. 2.—EXPERIMENT II.



Date.	Flask.	Titration value.	Titration of standard glucose solution.	R.	Conversion.
March 2 (after-noon).	f A	5.9 × 2	4.6	39	0.8 per cent.
	(B	6.7	4.6	30.2	49.1 „
March 3 (morning) after 18 hours.	f A	7.3	4.65	64	41.5 per cent.
	(B	6.3	4.65	73.8	57.5 „
March 4 (morning).	f A	6.4	4.65	72.7	56 per cent.
	(B	6.0	4.65	77.5	63.5 „
March 6 (morning).	f A	5.8	4.65	80.2	68 per cent.
	(B	5.6	4.65	83	72.5 „
March 8 (morning).	f A	5.5	4.65	84.6	75 per cent.
	(B	5.4	4.65	86.1	77.5 „
March 11 (morning).	f A	5.3	4.65	87.7	80 per cent.
	(B	5.3	4.65	87.7	80 „
March 15 (morning).	f A	5.3	4.7	88.7	81.5 per cent.
	(B	5.3	4.7	88.7	81.5 „

$$\begin{aligned} \text{Initial velocity for A} &= \frac{41.5 - 0.8}{57.5 - 49.1} = \frac{40.7}{8.4} = 4.85. \\ \text{Initial velocity for B} & \end{aligned}$$

The hindering effect is shown more graphically in Figures 3 and 4 of Experiments III and IV. The scheme adopted in these experiments is rather different from that of Experiments I and II. Two flasks, A and B, each contain at the beginning of the experiment the same concentration of maltose and the same concentration of enzyme; in A, however, there is, in addition, glucose of like concentration to the maltose. If glucose had no hindering effect, the rate of hydrolysis of maltose in each flask should be the same. It is seen, however, to be very much slower in the flask to which the glucose was added.

In Figures 3 and 4 it will be noticed that, besides the conversion curves of A and B, there is a third tracing called the glucose curve of A. This represents simply the percentage of glucose in the flask, and is the curve actually given by the estimations, the conversion curve of the maltose in flask A being derived from it by deducting 50 for the added glucose, and, of course, doubling the remainder. For example, if the estimations showed that of the total sugar in the flask A, 60 per cent. was glucose and 40 per cent. was maltose, it would mean that 20 per cent. of the original maltose had been hydrolysed. For flask B, the glucose curve coincides with the conversion curve.

#### EXPERIMENT III. (See Fig. 3, p. 647.)

*Sugar concentration in A*, 4 per cent.

*Sugar concentration in B*, 2 per cent.

*Maltose hydrate concentration in each flask*, 2 per cent.

*Temperature of bath*, 36°.

Flask A.....	{	0.997 gram of maltose hydrate.
		1 gram of glucose.
		1 c.c. of enzyme solution.
		Water to 50 c.c.
		Toluene.
Flask B.....	{	1.994 grams of maltose hydrate.
		2 c.c. of enzyme solution.
		Water to 100 c.c.
		Toluene.

The flasks were closed with rubber stoppers. For titration, 5 c.c. from flask A were alkalisied with 1 c.c. of a 2 per cent. sodium hydroxide solution and made up to 100 c.c., and 10 c.c. from flask B were alkalisied with 1 c.c. of a 2 per cent. sodium hydroxide solution and made up to 100 c.c. The time of boiling was 3 minutes, and the relative reducing powers of glucose and maltose hydrate were 100 and 38 respectively.

Date.	Flask.	Titration value.	Titration of standard glucose solution.	R.	Percentage of glucose in total sugar.	Percentage of maltose converted to glucose.
June 24 (morn- ing).	A	6.8	4.7	69.1	50	0
June 24 (1 p.m.)	B	6.05 × 2	4.7	38.8	1	1
June 24 (5 p.m.)	B	4.7 × 2	4.65	49.5	18	18
June 25 (noon).	f A B	6.2 7.0	4.7 4.7	75.8 67.2	61 47	22 47
June 26.	f A B	6.0 6.2	4.7 4.7	78.3 75.8	65 61	30 61
June 28.	f A B	5.75 5.7	4.7 4.7	81.7 82.5	70.5 72	41 72
July 12.	f A B	5.45 5.4	4.7 4.7	86.2 87	77.5 79	55 79
July 12.	f A B	5.1 5.05	4.7 4.7	92.1 93.1	87 89	74 89
July 19.	A	5.05	4.7	93.1	89	78
July 19.	A	by polarimeter, $[\alpha]_D$ at 23° = 60°; total glucose, 90 per cent.				

## EXPERIMENT IV. (See Fig. 4, p. 648.)

*Sugar concentration in A, 20 per cent. (approx.).**Sugar concentration in B, 10 per cent. (approx.).**Maltose hydrate concentration in each flask, 10 per cent. (approx.).**Temperature of bath, 30°.*

Flask A. ....	{	4.79 grams of maltose hydrate.
		4.88 grams of glucose.
		5 c.c. of enzyme solution.
		Water to 50 c.c.
		Toluene.



FIG. 3.—EXPERIMENT III.

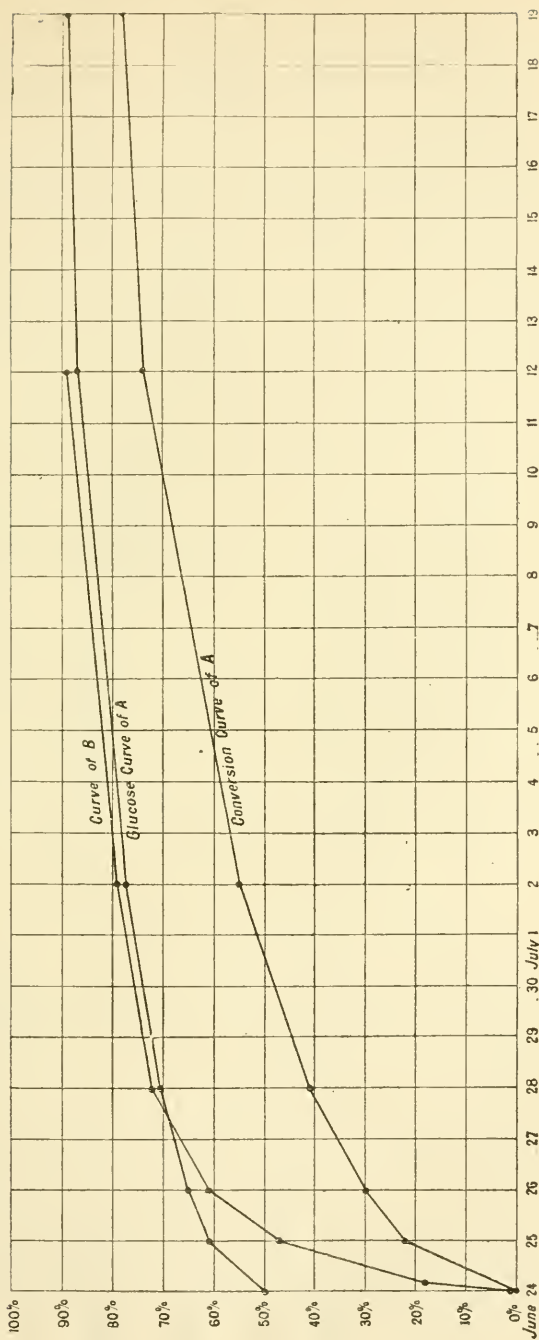
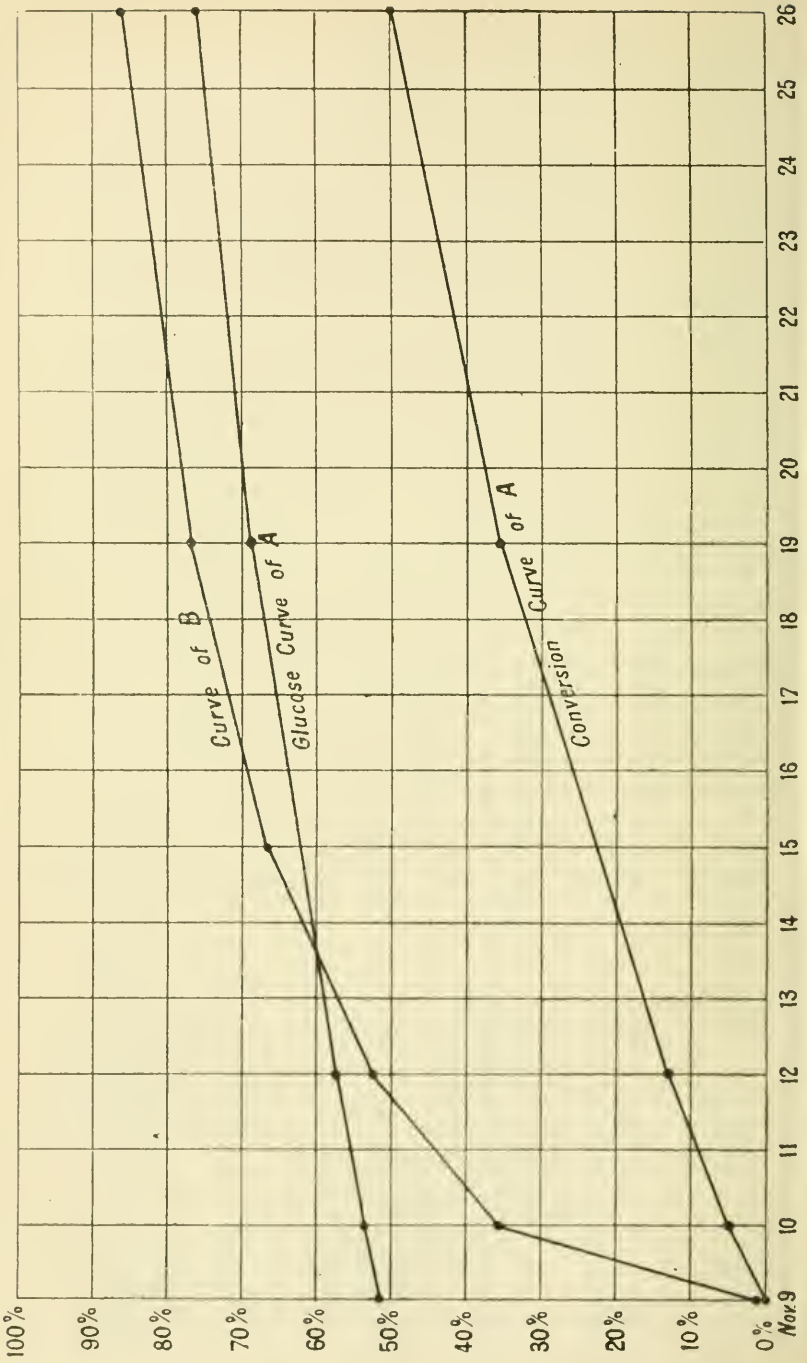


FIG. 4.—EXPERIMENT IV.



Flask B. ....	{	8.7 grams of maltose hydrate.
		10 c.c. of enzyme solution.
		Water to 100 c.c.
		Toluene.

All the solutions were sterilised and mixed under aseptic conditions, and all apparatus which came in contact with the solutions during the course of an experiment were also carefully sterilised; the flasks were closed with rubber stoppers. For the polarimetric determinations, 2 c.c. were taken from flask A, alkalisied and diluted to 20 c.c.; from flask B, 5 c.c. were taken, alkalisied, and diluted to 25 c.c. The concentration of the diluted solution, therefore, in the case of flask A, was 1.914 per cent. and the specific rotatory power was obtained from the rotation observed in a 200 mm. tube by multiplying the readings by 26.125. In the case of flask B, the concentration was 1.94 per cent. and the readings were multiplied by 25.75. The temperature of the water jacket was 15°. The specific rotatory powers of maltose hydrate and glucose in 2 per cent. concentration at this temperature were taken as 131.1° and 52.6° respectively.

For the titration, 10 c.c. taken from the polarimeter tube were diluted to 100 c.c. The concentrations of the solutions in the burette in the case of A and of B were 0.1914 per cent. and 0.194 per cent. respectively, and since the concentration of the standard glucose solution against which the titrations were made was 0.2 per cent., the multipliers 1.045 and 1.03 were introduced as corrections in the calculation of the reduction factors. The boiling was continued for 3 minutes. The percentage of maltose converted to glucose in flask A was obtained from the determination of total glucose by deducting the initial 51 per cent. and doubling the remainder. The results are given in the table, p. 650.

#### PART IV. THE REVERSE ACTION.

It has been shown in Part III that the presence of glucose hinders the hydrolytic decomposition of maltose by maltase, and it will have been noticed that the effect is more marked in those experiments in which the sugar solutions are more concentrated. The following experiments show that this appearance of a hindering effect is due to a reverse action by which glucose undergoes change with synthetic production of maltose. It will be seen that in presence of the enzyme solutions of glucose of sufficient concentration there is increase in optical activity and decrease in cupric-reducing power, the magnitudes of these changes having to one another the relation required on the assumption that glucose is converted to maltose. No change takes place in control flasks, so that the presence of the active enzyme is as

## EXPERIMENT IV.

Date.	Flask.	Observed rotation.	$[\alpha]_D$ .	Percentage glucose in total sugar.	Titration value.	Titration of standard glucose.	Z.	Percentage of glucose in total sugar.	Mean of the two methods.	Percentage of maltose converted.
November 9	A	3° 28'	90.6°	51.5	7.0	4.65	$\frac{4.65}{7} \times 100 \times 1.045 = 69.5$	50.5	51	0
November 9	B	5 2	130	1	6.3 × 2	4.65	$\frac{4.65}{6.3 \times 2} \times 100 \times 1.03 = 38$	0	0.5	0.5
November 10	A	3° 24'	88.8°	54	6.85	4.65	$\frac{4.65}{6.85} \times 100 \times 1.045 = 71$	53	53.5	5
November 10	B	4 0	103	36	8.0	4.65	$\frac{4.65}{8} \times 100 \times 1.03 = 60$	35.5	35.75	35.75
November 12	A	3° 18'	86.2°	57	6.55	4.65	$\frac{4.65}{6.55} \times 100 \times 1.045 = 74$	58	57.5	13
November 12	B	3 28	89	53	6.75	4.65	$\frac{4.65}{6.75} \times 100 \times 1.03 = 71$	52	52.5	52.5
November 15	B	3° 3'	78.5°	67	5.85	4.5	$\frac{4.5}{5.85} \times 100 \times 1.03 = 79$	66.5	66.75	66.75
November 19	A	2° 56.5'	76.8°	69	5.85	4.5	$\frac{4.5}{5.85} \times 100 \times 1.045 = 80.5$	68.5	68.75	35.5
November 19	B	2 44.5	70.5	77	5.45	4.5	$\frac{4.5}{5.45} \times 100 \times 1.03 = 85$	76	76.5	76.5
November 26	A	2° 44'	71.4°	76	5.7	4.65	$\frac{4.65}{5.7} \times 100 \times 1.045 = 85$	76	76	50
November 28	B	2 30	64.4	85	5.2	4.65	$\frac{4.65}{5.2} \times 100 \times 1.03 = 92$	87	86	86

essential for the reverse action as for the ordinary hydrolysis ; neither does a solution of the enzyme in absence of sugar develop of itself any such changes.

When the time allowed for the progress of the reaction is much extended, in order to find the limit of the conversion, the same equilibrium point is approached whether maltose is being hydrolysed to glucose or glucose synthesised to maltose, provided always that the concentration of total sugar is the same in each case.

The position of the equilibrium point is a function of the concentration, moving with increase of the latter in the direction of more maltose and less glucose ; for example, a solution of maltose of 4 per cent. concentration or less does not arrive at equilibrium point until nearly the whole is converted into glucose, whilst with solutions of 40 per cent. concentration there is some considerable amount of maltose present when close to the equilibrium point.

No attempt has been made to separate the synthesised maltose from the excess of glucose with which it is mixed ; but the osazone was separated from its mixture with glucosazone and identified, and it is hoped that the separation of the sugar itself will shortly be effected.

In the first experiment on the effect of adding a solution of the enzyme to a solution of glucose, a 20 per cent. concentration was used. Here the change was very small and the progress of the reaction slow, for in nineteen days the specific rotation had only increased by  $1^{\circ}$ , corresponding with a back conversion of 1.2 per cent. of the total sugar. The actual change in the observed rotation was  $5'$ , or ten times the probable error in reading, and no change could be detected in the control flask ; both these results were confirmed by several separate estimations. In the next experiment, a 40 per cent. concentration was used and a back conversion of 7.5 per cent. was noted, the value given by the copper method agreeing with the polarimetric to the nearest whole number. In Experiment VIII, of which details are appended, a freshly-prepared enzyme solution was used with a glucose concentration of 40 per cent. and a sufficient time was allowed for the reaction to be nearly completed. As much as 14.5 per cent. back conversion occurred in one flask and 15.5 per cent. in another in which the action was more rapid from the presence of a larger proportion of the enzyme ; and it is probable, from this and from Experiment IX, in which the equilibrium point was approached from the other side, that at this concentration there is equilibrium when 16 per cent. of the whole sugar is present as maltose (hydrate).

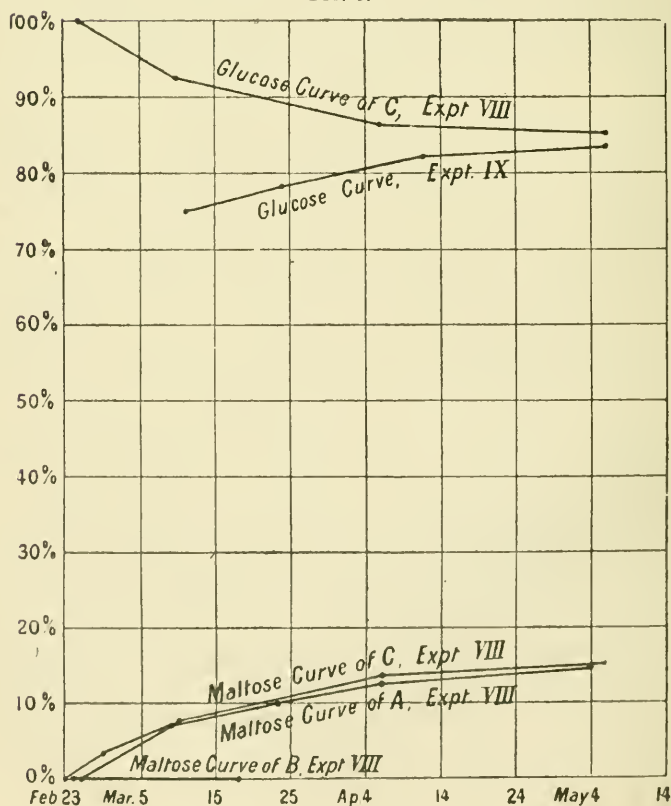


## EXPERIMENT VIII (See Fig. 5).

*Sugar concentration, 40 per cent. (approx.).**Temperature of bath, 30°.*

Flask A. ....	<div> 9.81 grams of glucose.  5 c.c. of enzyme solution.  Water to 25 c.c.  Toluene. </div>
Flask B. .... (control)	<div> 3.98 grams of glucose  2 c.c. of enzyme solution  Water to 10 c.c.  Toluene. </div> } boiled.
Flask C. ....	<div> 19.65 grams of glucose.  15 c.c. of enzyme solution.  Water to 50 c.c.  Toluene. </div>

FIG. 5.



## EXPERIMENT VIII.

Date.	Flask.	Weight of the 1 c.c. withdrawn.	Weight of sugar in 20 c.c. for polarimeter in 200 c.c. for titration.	Observed rotation.	$[\alpha]_D$	Percentage of glucose converted in- to maltose.	Titration value.	Titration of 0.2 per cent. standard glucose.	R.	Percentage of glucose converted into maltose.	Mean of the two methods.
February 23.	A	grams. 1.148	0.3925	2.06°	52.5°	0	$\left\{ \begin{array}{l} 4.8 \\ 4.75 \end{array} \right\}$	4.85	100.5	0	0
February 28.	A	1.147	0.392	2.16°	55°	3	4.7	4.55	97.7	3.5	3.25
March 9.	A	1.150	0.393	2.29°	58.3°	7.4	4.95	4.65	95.8	6.8	7
March 23.	A	1.148	0.3925	2.36°	60.3°	10	5.1	4.7	94	10	10
April 6.	A	1.152	0.394	2.47°	62.7°	13	5.05	4.6	92.5	12	12.5
May 4.	A	1.159	0.396	2.52°	63.6°	14	5.3	4.75	90.6	15	14.5
February 24.	B	1.148	0.398	2.08°	52.3°	0	4.7	4.7	100.5	0	0
March 17.	B	1.146	0.3975	2.075°	52.2°	0	$\left\{ \begin{array}{l} 4.4 \\ 4.45 \end{array} \right\}$	4.4	99.9	0	0
February 25.	C	1.1475	0.393	2.06°	52.4°	0	4.8	4.75	100.8	0	0
March 10.	C	1.148	0.393	2.315°	59°	8	5.05	4.75	95.7	7	7.5
April 6.	C	1.148	0.393	2.46°	62.6°	13	5.15	4.6	91	14	13.5
May 4.	C	1.151	0.394	2.52°	64°	14.5	5.4	4.8	90.4	15.5	15



*The Equilibrium Points.*

While the limit reached in Experiment IX was 83.25 parts of glucose to 16.75 parts of maltose hydrate, in Experiment VIII it was 15 parts of maltose hydrate to 85 parts of glucose; and, since in these experiments the equilibrium point was approached from opposite sides, its position must lie somewhere between these points, and not far from 84 parts of glucose to 16 parts of maltose hydrate. The flasks A and B in Experiment IV, with concentrations of 20 per cent. and 10 per cent. respectively, were allowed to remain in the bath at 30° for some months after the period mapped in Figure 4, until all action appeared to have stopped; the limits then reached were 90.5 per cent. for the 20 per cent. concentration, and 94.5 per cent. of glucose for the 10 per cent. concentration. In another experiment with 4 per cent. concentration, 98 per cent. of the maltose hydrate was converted into glucose, and with 2 per cent. concentration 99 per cent. has been converted. These results may be tabulated thus.

Sugar concentration.	Percentage of maltose hydrate hydrolysed to glucose.
40 per cent.	About 84
20     "	At least 90.5
10     "	"     94.5
4     "	"     98
2     "	"     99

In dilute solutions, therefore, hydrolysis is practically complete; with a concentration of 20 per cent., a reverse action can be detected; and with a concentration of 40 per cent., it is well marked.

*The Osazone.*

In each of the experiments made to test the reverse action, a part of the contents of the flask was treated with phenylhydrazine, and a more soluble osazone separated from the excess of glucosazone by extraction and recrystallising; the osazone had, in each case, the crystalline character of maltosazone. Examination of the control flasks gave a negative result. In Experiment VIII, a more extended examination of this osazone was made. It was prepared as follows: a portion of the contents of the flask was diluted with twice its volume of water, a few drops of acetic acid added, and the whole boiled on the water bath until a clear filtrate could be obtained. It was then treated on the water bath with phenylhydrazine hydrochloride and sodium acetate, the volume being such that the total sugar was in a concentration of about 10 grams in 150 to 170 c.c. The mixture quickly became almost solid from separation of glucosazone, which was three

times filtered off on a hot funnel. The solution, having been at the boiling point for  $1\frac{1}{2}$  hours in all, was then allowed to cool in the water bath, and the crystals, which separated on cooling, were extracted with boiling water, and the soluble part recrystallised, this process being repeated; crystalline plates resembling those of ordinary maltosazone were finally obtained. There was, however, more tendency for these plates to be deposited around a central axis than was observed in an osazone prepared from pure maltose, but not differing in this respect from a maltosazone prepared from a trial mixture of

FIG. 6.



pure maltose and glucose, 1 part of the former to 9 of the latter, to which also some boiled enzyme solution had been added in the proportion usual in the preceding experiments (see Fig. 6).

The osazone prepared from Experiment VIII, when the proportion of synthesised maltose had reached 10 per cent., melted at  $174-176^{\circ}$ , and another preparation, perhaps further purified, at  $178-180^{\circ}$ . The osazone made from the test mixture, containing ordinary maltose, melted at  $173^{\circ}$ , and that from Experiment VIII, when the proportion of synthesised maltose had reached 14 to 15 per cent. of the total sugar, at  $186^{\circ}$ . All these osazones showed signs of change below these temperatures, although in each case the bulk melted suddenly at the temperature given. When it is considered how greatly the melting point of maltosazone is depressed by a small amount of impurity,  $186^{\circ}$  is not lower than might be expected in the circumstances under which the substance was obtained. The melting point of maltosazone first given by Fischer was  $193^{\circ}$ , and afterwards  $206^{\circ}$ , whilst the melting point of isomaltosazone is about  $150^{\circ}$ .

Analysis of the osazone of the synthesised sugar by combustion with the aid of a Sprengel pump, gave the following results.

Osazone.	CO <sub>2</sub> at 0° and 760 mm.	N <sub>2</sub> at 0° and 760 mm.	Percentage of carbon.	Percentage of nitrogen.	Ratio C : N.
0.0325 gram	33.3 c.c.	2.7 c.c.	55.3	10.46	5.29
0.035 gram	35.9 c.c.	3.1 c.c.	55.3	11.1	4.98
Calculated for maltosazone .....			55.4	10.77	5.14
Calculated for glucosazone.....			60.4	15.65	3.86



It is, therefore, the osazone of a sugar of the  $C_{12}H_{22}O_{11}$  class. The possibility of its being isomaltosazone is excluded by its solubility in water at  $100^{\circ}$ , its melting point, and its crystal form, in each of which particulars it differs widely from isomaltosazone, and resembles ordinary maltosazone.

*Summary of Evidence for the Reverse Action.*

1. The hydrolysis of maltose by the enzyme is hindered by the presence of glucose. It is incomplete, and both these effects are more marked the more concentrated the solution.

2. When a concentrated solution of glucose is treated with the enzyme, the optical activity increases *pari passu* with a decrease in reducing power, the amounts of these changes having that mutual relation which is required on the assumption that glucose disappears and maltose is formed.

3. The same equilibrium point is approached whether one starts with a solution of maltose or with a solution of glucose of the same concentration.

4. When the presence of synthesised maltose has been tested by the use of phenylhydrazine, an osazone has been obtained having the percentage composition and the ordinary physical characteristics of maltosazone.

A reverse action in the case of the zymolysis of maltose suggests that other enzyme actions are also reversible. In the majority of cases it is very doubtful whether such reverse action would admit of demonstration, for even in the present case the sugar solution must be of high concentration, and in the cases where the substances are of high molecular weight and where the products of the hydrolysis are heterogeneous, the concentration would probably have to be far higher than could be attained.

As to whether the reverse action occurs in living cells, it is worth while pointing out that it is by no means necessary for a high concentration to be realised; it is only necessary for the synthesised product to be removed, perhaps by further synthesis through the agency of another enzyme, the process being repeated until an insoluble substance is formed. To take a concrete example: in the animal body glucose is present, also an enzyme capable of hydrolysing maltose, but no maltose is found. The hydrolysis of maltose takes place extra-cellularly in the alimentary canal; it is possible that the reverse process takes place intra-cellularly, the maltose being further dealt with as fast as it is formed, so that its concentration is kept practically nil. Many applications of this idea in physiology and

pathology suggest themselves but will be reserved for future investigation.

Part of the expenses of this research were defrayed by a grant from the Government Grants Committee of the Royal Society. I desire to record my thanks to this Committee and also to the Committee of the Davy-Faraday Laboratory of the Royal Institution for allowing me the use of a laboratory and of the greater part of my apparatus. The earlier part of the work was done in the Medizinisch-Chemisch. Institut, Bern, by the kind permission of the late Professor Drechsel.

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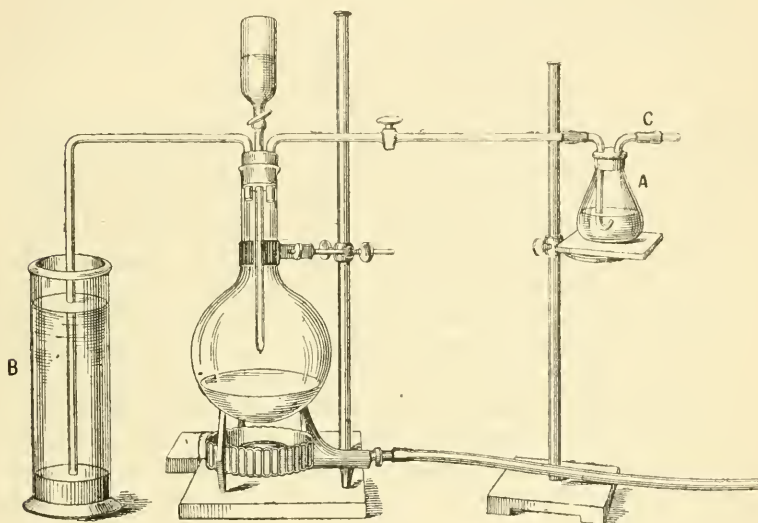
## LXVII.—*Preparation of a Standard Acid Solution by direct absorption of Hydrogen Chloride.*

By G. T. MOODY.

A VERY rapid and accurate method of preparing a standard acid solution consists in absorbing gaseous hydrogen chloride in water, determining the increase in weight, and subsequently diluting to a known bulk. The absorption is conveniently carried out in a conical flask, *A*, having a capacity of about 80 c.c. The flask is closed by a glass stopper, through which pass two tubes, one ending immediately beneath the stopper; the other, through which the gas is admitted, reaching nearly to the bottom of the flask, and having its end drawn out to a fine point and turned upwards. The upper ends of the tubes are bent at right-angles in opposite directions, and are fitted with rubber ends and light glass caps. The hydrogen chloride is generated either by heating fused salt or clear rock salt with a large excess of sulphuric acid, or by allowing pure sulphuric acid to drop into commercial muriatic acid. If the first of these methods is employed, no drying apparatus is necessary; but the gas prepared from muriatic acid is moist, and must be dried by passing it through a U-tube containing pumice moistened with sulphuric acid. In either case, a 'blow-off' arrangement, *B*, is necessary, the surplus gas passing through a mercury seal and dissolving in water.

When a steady stream of gas is being evolved, and the generating flask is known to be free from air by the evolved gas dissolving completely in water, the absorption flask, *A*, containing about 40 c.c. of water and previously weighed, is attached to the generating flask, and the gas turned on. A piece of glass tubing is then joined to the

rubber tube terminating the second tube, *C*, of the absorption flask, and by gently sucking, a slight vacuum is produced in the absorption flask; the rubber is then pinched and the glass cap replaced, whereby the contents of the flask remain under reduced pressure. After three or four minutes absorption, during which the absorption flask may be cooled by immersion in water, the rubber connecting the generating flask with the absorption flask is gently pushed off the tube leading from the generating flask, and the reduced pressure in the absorption



flask leads to the gas contained in the tube being immediately absorbed without water passing up the tube. The absorption flask, *A*, is then cooled and weighed, and the contents of the flask, and all acid adhering to the stopper and tubes, is washed into a half-litre flask and made up to bulk. From 2 to 4·8 grams of gas are absorbed in 3 minutes. The whole operation is extremely simple, and the accuracy of the method may be judged by the following numbers.

	Weight of gas absorbed.	Wt. of acid given by precipitation of aliquot part with silver nitrate.	Wt. of acid given by titration against precipitated $\text{CaCO}_3$ .
Experiment 1.....	2·942	2·939	
2.....	3·117	3·103	
3.....	3·019	3·016	3·017
4.....	3·875		3·869
5.....	3·0487	3·037	3·036
6.....	2·9016	2·9007	

In generating hydrogen chloride for absorption from salt, commercial oil of vitriol may be used ; but if the gas be prepared from muriatic acid, it is desirable to have the sulphuric acid free from nitric acid.

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## LXVIII.—*Constituents of the Indian Dyestuff Waras, Flemingia congesta.*

By ARTHUR GEORGE PERKIN, F.R.S.E.

DURING the investigation of kamala (*Mallotus Philippinensis*) (Trans., 1893, 63, 975 ; 1894, 65, 232), my attention was directed to an Indian product termed "waras," \* which, in its general reactions, closely resembled this dyestuff. Application was at that time made to the authorities of the Imperial Institute for a supply of this material, but although they have taken much trouble to fulfil this request they have only been able, owing to the scarcity of the drug, to place in my hands during the past few weeks about  $3\frac{1}{2}$  ounces for investigation. As the prospect of obtaining a further quantity was very remote, this was submitted to examination with the hope of isolating its principal constituents, and determining if these resembled, or were in any way related to, those present in kamala. The work must be considered obviously to partake more of the nature of a preliminary notice than a full investigation.

Waras consists of a purplish, resinous powder, which covers the seed pods of *Flemingia congesta*, an erect, woody shrub growing in the thickets and forests of the warmer part of India. According to Watt (*Dictionary of Economic Products of India*, vol. iii, p. 482), it is collected in Africa also, in the neighbourhood of Harrar, and is sent to Arabia, chiefly to Yemen and Hadhramant, where it is used as a dye, as a cosmetic, and as a specific against cold. Here, however, it is spoken of as a red powder, which is peculiar, for my own sample and one I have seen in the collection of Sir Thomas Wardle of Leek, has a purplish colour, as mentioned above. According to Sir Thomas Wardle (*ibid.*), waras is a distinctly inferior dye to kamala, and contains only a small amount of colouring matter compared with the yellow vegetable dyes of commerce. It is suitable as a dye for silk rather than for wool, but is quite useless with cotton. It has been introduced into England from Aden, as an adulterant or substitute for kamala (Flückiger and Hanbury's *Pharmacographia*, 1879, 576). Under the

\* Also named "wars" and "wurrus."

microscope, waras appears as transparent, orange-brown lumps, frequently circular and closely resembling kamala. Further, when destructively distilled, the pungent, acrid odour which is so characteristic of kamala when similarly treated is at once noticed. With alcohol, it yields an orange-coloured extract, and with dilute alkalis an orange-brown solution.

#### EXPERIMENTAL.

Waras was thoroughly extracted with carbon bisulphide in a Soxhlet's apparatus (extract A), and when dry with chloroform in the same manner, the latter operation requiring about three days. The chloroform extract left overnight deposited a finely divided, reddish precipitate (crude high melting resin), which was collected on the pump and washed with chloroform. The filtrate, on spontaneous evaporation, gradually deposited a reddish product similar to the above, but of a more sandy or less gelatinous character; this was collected, washed with chloroform, dissolved in boiling toluene, and the crystalline powder which separated on cooling was recrystallised in the same manner, employing animal charcoal. It was, however, not always possible to so readily isolate this crystalline principle, the product being sometimes contaminated with a resin which impeded crystallisation; when this occurred, it was again dissolved in excess of chloroform, that which separated immediately on cooling being rejected, and the deposits obtained by the fractional evaporation of the filtrate examined in turn as to their crystalline property. The substance appeared to be pure when its hot toluene solution, on cooling, did not become opaque before the crystals separated. About 3 grams were thus prepared.

0.1087 gave 0.2816  $\text{CO}_2$  and 0.0628  $\text{H}_2\text{O}$ .  $\text{C} = 70.65$ ;  $\text{H} = 6.41$ .

0.1024 „ 0.2640  $\text{CO}_2$  and 0.0547  $\text{H}_2\text{O}$ .  $\text{C} = 70.31$ ;  $\text{H} = 5.93$ .

$\text{C}_{12}\text{H}_{12}\text{O}_3$  requires  $\text{C} = 70.59$ ;  $\text{H} = 5.88$  per cent.

*Flemingin*, which is the name proposed for the substance thus obtained, is a dull, orange-red, crystalline powder, having a faint lustre, and, under the microscope, is seen to consist of star-shaped groups of small prismatic needles. In appearance it could be readily mistaken for rottlerin, the principal crystalline constituent of kamala, although the latter is paler, and is of a more salmon-coloured tint. It is sparingly soluble in hot toluene and chloroform, almost insoluble in carbon bisulphide, but *readily soluble* in cold alcohol and acetic acid, the latter properties distinguishing it from rottlerin, which is only sparingly soluble in these liquids even when boiling. Solutions of the alkaline hydroxides dissolve it in the cold with a deep, orange-red, brown tint (rottlerin dissolves with an orange coloration), and these solutions



when boiled, although evidently suffering gradual decomposition, do not deposit resinous matter as is the case with rottlerin. It is soluble in sodium carbonate solution only on gentle warming. When heated, it melts at  $171\text{--}172^\circ$  (rottlerin at  $198\text{--}200^\circ$ ), and when destructively distilled evolves a pungent acrid odour, whilst a thick, brown oil condenses, properties which are also characteristic of rottlerin. In some other properties also it resembles the latter, for both give a brownish-black coloration with alcoholic ferric chloride, and the alkaline solutions in each case are decolorised by zinc dust.

*Dyeing Properties.*—It will be remembered (*loc. cit.*) that the dyeing properties of rottlerin in regard to silk and wool are only exhibited by its solutions in hot alkali carbonates, and its behaviour in this respect is not due to the deposition of rottlerin on the fibre, but of one or other of the decomposition products which result from the action of the alkali; this decomposition is preceded by the formation of a sparingly soluble alkali salt, which is then decomposed, principally into a substance I have termed rottlerone.

Experiment showed that flemingin possessed similar properties. Silk suspended in a solution of the substance in dilute sodium carbonate, and the whole gradually raised to boiling heat, was dyed golden yellow, slightly duller than the shade given by rottlerin. Comparative dyeing trials between these colouring matters (0.05 gram of each, 1 gram  $\text{Na}_2\text{CO}_3$  and 70 c.c. water) indicated that flemingin possessed much stronger dyeing power than rottlerin; for instance, strips of silk, 0.24 gram each, were inserted into each dye vessel, and withdrawn when a full shade was produced, others being put in their place, and although the bath containing flemingin dyed six of these, and even then was unexhausted, the rottlerin gave a satisfactory result with only one such strip. Evidently, therefore, flemingin is more slowly decomposed by the hot carbonate solution, or the decomposition products are soluble in the alkaline liquid, whereas rottlerin is well known to be rapidly attacked with the formation of substances insoluble in this reagent.

*Decomposition with Fused Alkali.*—Flemingin was heated with about 20 times its weight of potassium hydroxide and a little water at  $160^\circ$  for 45 minutes; it did not dissolve completely, a dark, brown resinous matter floating on the liquid, a behaviour characteristic of rottlerin and the resinous constituents of kamala. The melt was dissolved in water, and the brown solution neutralised with acid, when a dark, resinous precipitate separated, and there was a pungent odour of acetic acid. The mixture was then extracted with ether, the extract evaporated, the brown, sticky residue extracted with boiling water, and the solution neutralised with sodium hydrogen carbonate and again extracted with ether. From the aqueous liquid after acidification, ether

removed a crystalline product in very small quantity, which was found to consist of two substances; these were separated as follows. An ethereal solution of the residue was diluted with its own bulk of light petroleum (b. p. 60—80°), and the mixture evaporated until the liquid became cloudy, and on cooling deposited indistinct crystals; these were collected (the filtrate reserved) and recrystallised from benzene. The product consisted of pale yellow, microscopic needles melting at 182—184°, although not sharply; with ferric chloride, it gave a deep violet coloration. On sublimation, colourless needles were obtained, but here evidently decomposition takes place, for these begin to melt at 150°.

On evaporating the light petroleum solution from which the crystals had been deposited, long, colourless needles of *salicylic acid* were obtained melting at 155—156°, and giving a violet coloration with ferric chloride. The products of the action of alkali consists, therefore, of *salicylic acid*, *acetic acid*, and an acid of higher melting point, which, owing to lack of material, it was impossible to identify. Knowing that rottlerin contains a cinnamyl nucleus, the formation from *flemingin* of *acetic* and *salicylic acids* suggests as possible that this may be a crude *orthohydroxycinnamic acid*.

#### *The Resin of High Melting Point.*

The crude resin of high melting point (page 661) obtained during the isolation of *flemingin* was dissolved in a large bulk of boiling chloroform and the flaky deposit which separated on cooling treated again in a similar manner. It was finally crystallised (?) from toluene.

0.1186 gave 0.3082 CO<sub>2</sub> and 0.0637 H<sub>2</sub>O. C = 70.87; H = 5.96.

C<sub>12</sub>H<sub>12</sub>O<sub>3</sub> requires C = 70.59; H = 5.88 per cent.

The product was a brick-red powder which, when heated, showed signs of sintering at 133° and melted at 162—167°. Under the microscope, in the moist condition, it was seen as small, transparent, gelatinous nodules devoid of crystalline appearance, and all attempts to obtain it crystalline have hitherto been unsuccessful. In its behaviour with the alkali carbonates and hydroxides, it resembles *flemingin*, except in the colour of the solutions, which are distinguished by their strongly-marked brown tint. This is also readily observed in the dyeing properties of this resin, which are of a duller and more reddish tint than those given by *flemingin*. Fused with alkali at 200—220° there were formed a resinous product, *acetic acid*, and a colourless, crystalline acid which had the properties of *salicylic acid*.

The resin of high melting point is evidently closely allied to flemingin, but its properties are sufficiently characteristic to denote that it is not an impure form of that substance. It is present in small quantity only.

*The Yellow Crystalline Colouring Matter.*

The chloroform mother liquors from the purification of the above resin were allowed to evaporate spontaneously, and the precipitate which formed collected from time to time. The deposits first formed had the characteristics of the above resin, but eventually a very small quantity of a light yellow product separated; a solution of this in hot toluene, on cooling, became semi-solid from the separation of crystals, which were then recrystallised in a similar manner; 0.09 gram was thus obtained. Analysis gave C = 69.97; H = 5.75, numbers resembling those required by flemingin. It formed a lustrous, glistening mass of pale yellow needles melting at 165—166°, sparingly soluble in toluene, readily in alcohol. The alkali and alkali carbonate solutions dissolved it with an orange-red coloration, and with alcoholic ferric chloride it gave a brownish-black liquid. It is interesting to notice that kamala contains also a minute trace of an analogous substance which has been termed homorottlerin, and for the present it is proposed to distinguish this waras product as *homoflemingin*.

*The Resin of Low Melting Point.*

This substance, which is the principal constituent of waras, is present in considerable quantity in the chloroform mother liquors described above, and also in the carbon bisulphide extract (A). As flemingin itself is but little soluble in the latter solvent, it seemed probable that from this a pure substance could be more readily isolated.

Extract A, on cooling, deposited a somewhat sticky product from which a small amount of a crystalline substance resembling flemingin was isolated. The filtrate was then allowed to evaporate spontaneously, and any further precipitate which formed was removed. A transparent, vitreous residue was finally obtained, in which a wax was present; this could be removed by dissolving the mass in ether, and agitating the solution with very dilute alkali, in which the resin alone was soluble. The alkaline solution was now acidified, extracted with pure ether, the extract evaporated, and the residue dried at 110° until the weight was constant.

0.1175 gave 0.3075 CO<sub>2</sub> and 0.0672 H<sub>2</sub>O. C = 71.37; H = 6.35

C<sub>13</sub>H<sub>14</sub>O<sub>3</sub> requires C = 71.56; H = 6.42 per cent.

It consists of a transparent, brittle mass of a deep orange-brown colour melting below  $100^{\circ}$ , readily soluble in alcohol, ether, and chloroform, somewhat more sparingly in carbon bisulphide. The alkali hydroxides dissolve it with a coloration closely resembling that given by the resin of high melting point and it differs in this respect from the resin of low melting point, also present to a considerable extent in kamala the alkaline solutions of which have an orange tint. In other respects, however, it closely resembles the kamala product, and on dry distillation evolves a pungent odour, with condensation of a thick, brown oil so characteristic of this class of substance.

On fusion with alkali at  $200-220^{\circ}$ , a colourless, crystalline acid melting at  $155-156^{\circ}$ , identified as *salicylic acid*, and a resinous product were formed; the presence of *acetic acid* was also detected.

If kamala resin, and also rottlerin, be dissolved in nitric acid of sp. gr. 1.5, and the solution rapidly evaporated, paranitrobenzoic acid and oxalic acid are the chief products. Experiments carried out in a similar manner with the above substance yielded, however, *oxalic acid* only.

*Summary of Results.*—This investigation indicates that waras contains five distinct substances, namely, flemingin, homoflemingin, resins of high and low melting points, and a wax. Although these are not identical with any constituent of kamala, the analogy between these drugs is remarkable, for from the latter rottlerin, homorottlerin, a high and low melting resin and a wax can be isolated (*loc. cit.*). The products from both sources, moreover, have many special characteristics in common, and there can be but little doubt that a close chemical relationship exists between them. The kamala substances contain, as I have previously pointed out (*loc. cit.*), a cinnamyl nucleus and thus, by decomposition with alkali give benzoic and acetic acids; those from waras, on the other hand, yield in the same way salicylic and acetic acids, which suggests they may contain a hydroxycinnamyl group.

It should be pointed out that rottlerin has an exceedingly high molecular weight, namely 570, and although this is probably the case with flemingin and the accompanying substances, simple formulæ have been adopted until this can be put to proof.

*Dyeing Properties of Waras.*—Suspended in a boiling solution of its own weight of sodium carbonate, waras readily dyes silk golden-yellow shades very similar to those produced by kamala, but slightly duller and more orange. These are brightened by rinsing in very dilute acetic acid, and alkali carbonate solutions produce a slightly reddening effect. Material was not available for an extended study of its tinctorial properties, but it was at once evident that, in strength, waras



is a decidedly superior dyestuff to kamala. Whether it is capable of competition with the yellow dyestuffs of commerce cannot be determined until larger quantities can be procured for more extended work in this direction. In the meantime, I shall be grateful for information which will enable me to obtain a supply of this material.

CLOTHWORKERS' RESEARCH LABORATORY,  
DYEING DEPARTMENT,  
YORKSHIRE COLLEGE.

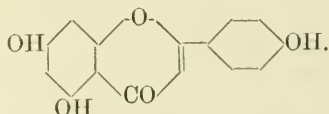
# LXIX.—*Azobenzene Derivatives of some Natural Yellow Colouring Matters: Apigenin, Chrysin, Morin, Euxanthone, and Gentisin.*

By ARTHUR GEORGE PERKIN, F.R.S.E.

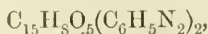
IN previous investigations, the azobenzene compounds of maclurin (Trans., 1897, 71, 186), cotoin, and phloretin (Trans., 1897, 71, 1149) have been studied, and it now appeared desirable to examine analogous derivatives of the allied flavone and xanthone groups. Of the former class, chrysin, apigenin, and morin were selected, with the object of accumulating further evidence as to their relationship, and, of the latter, euxanthone and gentisin were interesting for comparison, for it seemed probable that the position of the methoxy-group in gentisin could be thus determined.

## *Apigenin.*

A recent examination of this substance, the colouring matter of parsley (Trans., 1897, 71, 805), *Apium petroselinum*, revealed a striking similarity between its properties and those of chrysin; its behaviour with fused alkali specially indicated this resemblance, as it yielded phloroglucinol and parahydroxyacetophenone, and a study of its derivatives also pointed to the fact that it was an hydroxychrysin or trihydroxyflavone,



With diazobenzene, it formed disazobenzeneapigenin,



although at the time the properties of this compound were not fully examined. During its purification, for which acetic acid was partly



employed, a bye-product was isolated which had the characteristics of an acetyl derivative, and a notice of this substance was communicated to the Society (Proc., 1897, p. 54). Owing, however, to a lack of material necessary to establish its identity, it was not described in the full paper (*loc. cit.*), but reserved for further examination.

Crude disazobenzeneapigenin was extracted with alcohol to remove a resinous impurity, and subsequently with a boiling mixture of nitrobenzene and acetic acid until an orange-yellow mass of the almost pure disazo-derivative remained. The nitrobenzene extracts on cooling yielded no deposit, but when diluted with hot alcohol a crystalline product separated, which was collected and washed with alcohol.

0.1274 gave 0.3105  $\text{CO}_2$  and 0.0493  $\text{H}_2\text{O}$ .  $\text{C} = 66.47$ ;  $\text{H} = 4.29$ .

0.1266 „ 0.3095  $\text{CO}_2$  „ 0.0463  $\text{H}_2\text{O}$ .  $\text{C} = 66.66$ ;  $\text{H} = 4.06$ .

$\text{C}_{15}\text{H}_7\text{O}_5(\text{C}_2\text{H}_3\text{O})(\text{C}_6\text{H}_5\text{N}_2)_2$  requires  $\text{C} = 66.92$ ;  $\text{H} = 3.84$  per cent.

It formed a glistening mass of orange-red leaflets melting at  $259-260^\circ$  somewhat more soluble in nitrobenzene than the disazobenzene derivative itself, and insoluble in dilute alkali. As disazobenzeneapigenin is very sparingly soluble in alkaline solutions, owing apparently to the formation of an insoluble salt with the alkali, further proof was necessary to determine if this was in reality an acetyl compound. This appeared to be the case, for by decomposition with sulphuric acid, a process in which a purification does not occur, crystals of disazobenzeneapigenin melting at  $290-292^\circ$  were obtained; other preparations of this product gave a like result, but a slight variation in the melting point of each was observed; the yield, however, was very small and the process troublesome, and as it was likely that the acetyl compound contained traces of the unaltered substance, it was considered more advisable to study its preparation by the ordinary methods. The apigenin employed in these experiments was prepared from the glucoside apiin, by the method previously described (*loc. cit.*), the apiin being purchased from Merck of Darmstadt. A sample of the disazobenzene derivative,  $\text{C}_{15}\text{H}_8\text{O}_5(\text{C}_6\text{H}_5\text{N}_2)_2$ , on analysis, gave 11.38 per cent. of nitrogen, theory requiring 11.71 per cent.

In order to acetylate this product, 1 gram was boiled with 20 c.c. of acetic anhydride for 3 hours, but at the expiration of this time no action appeared to have taken place, although the crystals had a more glistening appearance; subsequent experiment showed, however, that a partial acetylation had occurred. Experiments were now carried out employing a very large excess of acetic anhydride, 150 c.c., the disazobenzene compound, 1 gram, being added to this in small portions at a time. A clear solution was gradually formed, but this on longer boiling commenced to deposit crystals, which, after 8 hours digestion, were collected, washed with acetic acid, and finally with alcohol. 0.733 gram was

thus obtained. In appearance and general properties, this product so closely resembled the original disazobenzene compound that at first it appeared doubtful whether reaction had taken place. Analysis, however, showed this to be incorrect.

0.1104 gave 10.5 c.c. nitrogen at  $18^{\circ}$  and 748 mm.  $N = 10.80$ .

$C_{15}H_7O_5(C_2H_3O)(C_6H_5N_2)_2$  requires  $N = 10.77$  per cent.

To corroborate this result, the substance, suspended in boiling acetic acid, was decomposed by sulphuric acid, and to the clear solution boiling water was cautiously added, the crystals of the free disazo-compound which separated being collected and weighed.

0.4020 gave 0.3680  $C_{15}H_8O_5(C_6H_5N_2)_2$ . Found 91.54.

0.6053 „ 0.5540 „ „ „ „ 91.52.

The theory for the loss of one acetyl group requires 91.92 per cent.

*Acetyl disazobenzeneapigenin* forms a glistening mass of orange-red needles insoluble in alkaline solutions, and is in appearance practically indistinguishable from the free disazo-compound, which is itself almost insoluble in these reagents. In their behaviour also with the usual solvents, no characteristic differences could be observed, although the acetyl compound is somewhat more readily dissolved by hot nitrobenzene. When rapidly heated, acetyl disazobenzeneapigenin melts at  $277-280^{\circ}$ , and if slowly heated at  $266-268^{\circ}$ , signs of decomposition appearing at about  $260^{\circ}$ ; on the other hand, disazobenzeneapigenin, when heated in a similar manner, melts at  $290-292^{\circ}$  and  $270-272^{\circ}$  respectively. So close a similarity between a substance and its acetyl derivative is unusual, and it thus appeared advisable to determine whether disazobenzeneapigenin is decomposed or suffers loss by treatment with a solution of sulphuric acid in boiling acetic acid. This was evidently not the case, for 0.7410 in this way gave 0.7382, or 99.60 per cent. of unaltered substance.

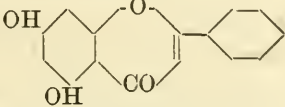
Finally, disazobenzeneapigenin was heated with acetic anhydride in a sealed tube at  $160-170^{\circ}$  for 4 hours, to determine if a more highly acetylated product could be obtained. The crystals which separated on cooling were collected and recrystallised from a mixture of nitrobenzene and alcohol.

It was identical in melting point and general properties with the monoacetyl derivative above described, and it is thus apparent that disazobenzeneapigenin contains but one free hydroxyl group. Consequently, apigenin itself would appear to contain three such, the diazobenzene groups in each case neutralising one of these, and this has been proved by the following examination of chrysin.

*Chrysin.*

Evidence was still required to prove with certainty the exact positions of the diazobenzenes in the apigenin compound, for this appears to contain, not only a phloroglucinol, but a phenol nucleus.

Chrysin, the colouring matter of poplar buds, has been shown by Kostanecki (*Ber.*, 1893, 26, 2901) to be a dihydroxyflavone of this

constitution,  and should this yield a

disazo-derivative the constitution of the apigenin compound would be at once evident.

Some chrysin was therefore prepared from poplar buds according to Piccard's method (*Ber.*, 1873, 6, 884), and a solution of this in dilute alkali treated with an excess of diazobenzene sulphate; the orange-red, gelatinous precipitate thus produced was collected, washed, dried, and repeatedly extracted with boiling alcohol, to remove a resinous product present in considerable quantity. The orange-coloured residue was dissolved in the least possible quantity of hot nitrobenzene, the solution mixed with half its bulk of alcohol, and the crystals which separated collected and washed with alcohol.

0.1175 gave 0.3022 CO<sub>2</sub> and 0.0430 H<sub>2</sub>O. C = 70.14; H = 4.06.

0.1138 „ 12 c.c. nitrogen at 22° and 752 mm. N = 11.81.

C<sub>15</sub>H<sub>8</sub>O<sub>4</sub>(C<sub>6</sub>H<sub>5</sub>N<sub>2</sub>)<sub>2</sub> requires C = 70.13; H = 3.89; N = 12.12 per cent.

*Disazobenzenechrysin* forms an orange-coloured, glistening mass of fine needles melting with decomposition at 251–252° when slowly heated. It is very sparingly soluble in boiling alcohol, somewhat more readily in acetic acid and nitrobenzene, and insoluble in alkaline solutions. Sulphuric acid dissolves it, giving a liquid of a scarlet colour. This substance, when boiled with acetic anhydride for 6 hours, remained unchanged, the crystals which separated on cooling giving the following results on analysis.

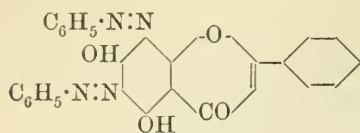
0.1042 gave 11.2 c.c. nitrogen at 21° and 752 mm. N = 12.10.

C<sub>15</sub>H<sub>8</sub>O<sub>4</sub>(C<sub>6</sub>H<sub>5</sub>N<sub>2</sub>)<sub>2</sub> requires N = 12.12 per cent.

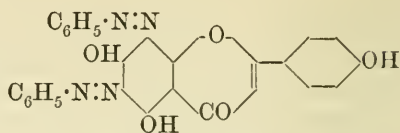
To be certain of this, however, the small quantity remaining, 0.2726 gram was digested with an acetic acid solution of sulphuric acid. The crystals which separated on dilution weighed 0.2703 gram, a yield of 99.15 per cent.

Disazobenzenechrysin, as was to be expected, cannot therefore be acetylated, and contains no free hydroxyl groups, consequently the

constitutions of disazobenzenechrysin and disazobenzeneapigenin may be thus represented.



Disazobenzenechrysin.

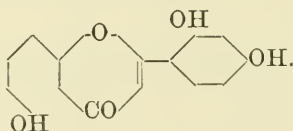


Disazobenzeneapigenin.

*Dyeing Properties.*—The properties of these two substances in this respect are very similar, although of little interest. Upon wool mordanted with chromium and on the unmordanted material, they gave respectively (a) red orange and orange, and (b) pale red-orange and pale orange shades. As was to be expected from the insoluble pigment-like nature of these products, a considerable portion of the colour of these patterns could be removed by mere friction.

#### *Morin.*

This substance, the principal colouring matter of old fustic (*Morus tinctoria*), has been shown in a recent communication (Trans., 1896, 69, 792) to possess properties closely in harmony with the following constitution.



On account of its analogy to the foregoing substances, a study of its behaviour towards diazobenzene was interesting; and some of the substance, prepared and purified by the methods previously described, was therefore dissolved in dilute alkali, and the solution treated with diazobenzene sulphate in excess of that necessary for the formation of a trisazo-derivative. A deep maroon-coloured product separated, which was collected, washed, dried, and extracted with boiling alcohol, to remove an easily soluble, somewhat resinous product, which is present in considerable quantity. To a solution of the residue in boiling nitrobenzene, alcohol was cautiously added, and the amorphous precipitate which separated on cooling was collected, washed with alcohol, and again dissolved in a very small quantity of nitrobenzene; on adding acetic acid, a crystalline powder separated, which was collected and washed with acetic acid.

0.1128 gave 11 c.c. nitrogen at 15° and 754 mm.  $N = 11.32$ .

$C_{15}N_8O_7(C_6H_5N_2)_2$  requires  $N = 10.98$  per cent.



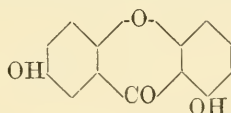
*Disazobenzene*morin is a red-brown powder, appearing under the microscope as warty nodules interspersed with rosettes of very minute needles. It is almost insoluble in hot alcohol or acetic acid, moderately soluble in nitrobenzene; sulphuric acid dissolves it with an orange-brown coloration. Cold dilute alkalis do not attack it, but on boiling it dissolves somewhat slowly, forming a brownish-red solution.

The yield of pure product obtained by the above method was exceedingly small, the main bulk consisting of the soluble resinous substance above referred to, and on this account its acetylation could not be properly studied without the employment of very large quantities of pure morin. It was ascertained, however, that, by digestion with acetic anhydride, an orange-coloured acetyl compound could be obtained. Morin, therefore, behaves similarly to apigenin in yielding a disazo-derivative, a point of interest, in that both substances containing, as they do, respectively phloroglucinol and resorcinol, and phloroglucinol and phenol nuclei, might be expected to form trisazo-compounds. The readily soluble, so-called resinous, products which are formed in each case when diazobenzene sulphate is added to an alkaline solution of these colouring matters could hardly contain trisazo-derivatives, for these are, as a rule, characterised by their sparing solubility. It is probable that, with this class of compound, these cannot exist, or that their production is at once followed by decomposition.

### *Euxanthone.*

Euxanthone is derived from the Indian dyestuff "purée" or piuri (*jaune indien*), a deposit obtained from the urine of cows and consisting of the magnesium salt of euxanthic acid; by treatment with hydrochloric acid, this is decomposed into euxanthone and glycuronic acid,  $C_{19}H_{18}O_{11} = C_{13}H_8O_4 + C_6H_{10}O_7$ .

Kostanecki and Nessler (*Ber.*, 1891, 24, 3980) have synthesised this substance by distilling resorcinol with quinolcarboxylic acid, and assign to it the following constitution as probable.



To a slightly alkaline solution of euxanthone, a solution containing diazobenzene sulphate (2 mols.) was added and the deep red precipitate was collected and washed. After extraction with boiling alcohol, the residue was suspended in boiling acetic acid, and nitrobenzene added drop by drop until a clear solution was obtained; on cooling, crystals separated which were collected and washed with alcohol.



0.1084 gave 12.6 c.c. nitrogen at 19° and 744 mm.  $N = 13.07$ .

$C_{13}H_6O_4(C_6H_5N_2)_2$  requires  $N = 12.85$  per cent.

*Disazobenzene-euxanthone* forms a glistening, brick-red mass of fine needles melting at 249—250° with decomposition, readily soluble in boiling nitrobenzene. It is insoluble in cold dilute alkali, and even on boiling is but little attacked, so that at first sight it seemed as if this substance contained no free hydroxyl groups. To determine whether this was the case, its behaviour with acetic anhydride was studied. It was very slowly attacked by this reagent, but eventually dissolved; after boiling the solution for 3 hours, and allowing it to cool, the addition of alcohol caused a separation of crystals, which were collected, and recrystallised first from acetic acid and finally from toluene.

0.1064 gave 10.2 c.c. nitrogen at 17° and 756 mm.  $N = 11.06$ .

$C_{13}H_4O_4(C_2H_3O)_2(C_6H_5N_2)_2$  requires  $N = 10.77$  per cent.

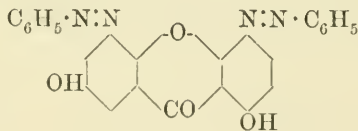
*Acetyl-disazobenzene-euxanthone* was obtained as a pale ochre-coloured mass of glistening needles melting at 197—199°, sparingly soluble in acetic acid, more readily in toluene. It is not attacked by cold alkaline solutions, and when boiled with them becomes red, a trace only dissolving. To determine with certainty the number of acetyl groups, it was decomposed with sulphuric acid in the manner previously described.

0.4307 gave 0.3643  $C_{13}H_6O_4(C_6H_5N_2)_2$ . Found 84.58. The theory for the loss of two acetyl groups requires 83.84 per cent.

The regenerated disazobenzene-euxanthone was analysed.

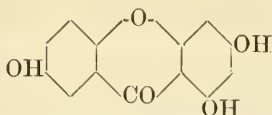
0.1228 gave 14.4 c.c. nitrogen at 20° and 749 mm.  $N = 13.21$ . Theory requires  $H = 12.85$  per cent.

Disazobenzene-euxanthone, like euxanthone itself, contains, therefore, two free hydroxyl groups, consequently the diazobenzene groups cannot be in the ortho-position relatively to these. Its most probable constitution is as follows.

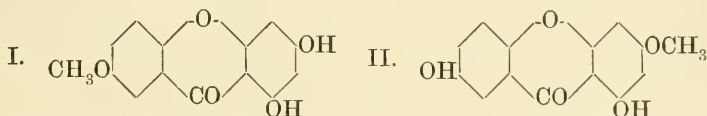


*Gentisin.*

This substance, the colouring matter of gentian root, has been investigated by Kostanecki (*Chem. Centr.*, 1891, i, 587), and found to be a monomethyl ether of gentiscin,  $C_{13}H_8O_5$ . As the latter when decomposed with alkali yields phloroglucinol and quinolcarboxylic acid, they assigned to it the constitution of a trihydroxyxanthone.



Subsequently Tambor and Kostanecki (*Monatsh.*, 1894, 15, 1—8) synthesised this substance by distilling phloroglucinol with quinol-carboxylic acid, and further by a partial methylation this yielded gentisin. Their experiments indicated as possible two formulæ for gentisin according to the position of the methoxyl group, of which the second here given seemed preferable.



As the true position of this group is still doubtful, it appeared to me that this could be indicated with certainty by a study of its azobenzene derivative.

Gentisin, procured from Merck of Darmstadt, was dissolved in dilute alkali, treated with excess of diazobenzene sulphate, and the bright red precipitate collected and dried. After extraction with alcohol, it was dissolved in hot acetic acid with the aid of nitrobenzene, and the crystals which separated on cooling collected and washed with alcohol. On analysis,

0.1175 gave 0.2878  $\text{CO}_2$  and 0.0448  $\text{H}_2\text{O}$ .  $\text{C} = 66.80$ ;  $\text{H} = 4.23$ .

0.1262 „ 13.7 c.c. nitrogen at  $15^\circ$  and 748 mm.  $\text{N} = 12.50$ .

0.1304 „ 14.1 c.c. „  $17^\circ$  „ 748 mm.  $\text{N} = 12.34$ .

$\text{C}_{14}\text{H}_8\text{O}_5(\text{C}_6\text{H}_5\text{N}_2)_2$  requires  $\text{C} = 66.95$ ;  $\text{H} = 3.86$ ;  $\text{N} = 12.02$  per cent.

*Disazobenzenegentisin* forms a glistening mass of scarlet needles melting at  $251\text{--}252^\circ$  with decomposition, readily soluble in hot nitrobenzene, almost insoluble in alcohol. Hot alkaline solutions dissolve it somewhat slowly, with formation of an orange-coloured liquid.

To acetylate this product, it was dissolved in hot acetic anhydride, and the solution boiled for 3 hours. On cooling, the addition of alcohol caused the separation of crystals, which were collected and crystallised, first from acetic acid, and finally from toluene.

0.1189 gave 10.2 c.c. nitrogen at  $19^\circ$  and 743 mm.  $\text{N} = 9.64$ .

$\text{C}_{14}\text{H}_6\text{O}_6(\text{C}_2\text{H}_3\text{O})_2(\text{C}_6\text{H}_5\text{N}_2)_2$  requires  $\text{N} = 10.18$  per cent.

To determine the acetyl groups with certainty, it was decomposed with sulphuric acid in the presence of acetic acid.

0.8803 gave 0.7538  $C_{14}H_8O_5(C_6H_5N_2)_2$ . Found 85.62.

0.7141 „ 0.6067 „ „ 84.96.

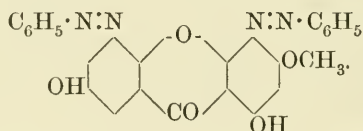
Theory for the loss of two acetyl groups requires 84.73 per cent.

The regenerated disazobenzenegentisin was analysed.

0.1182 gave 12.8 c.c. nitrogen at  $17^\circ$  and 743 mm.  $N = 12.27$ .

Theory requires  $N = 12.02$  per cent.

*Diacetyldisazobenzenegentisin* forms orange-red needles melting at  $218-220^\circ$ , moderately soluble in hot acetic acid, but only very sparingly in alcohol. It is not attacked by cold dilute alkali, but is decomposed by digestion at the boiling temperature. Disazobenzene-gentisin, therefore, like gentisin itself, contains two free hydroxyl groups, which cannot thus be in the ortho-position relatively to the diazobenzene groups. If formula I truly represented the constitution of gentisin, it should, like chrysin, form a disazobenzene derivative containing no free hydroxyl groups. From a substance of the constitution II, on the other hand, a diazobenzene derivative should result of a nature similar to that of euxanthone; this is the case, and II must, therefore, be the true constitution of gentisin. Disazobenzenegentisin may be thus represented.



Diazobenzene-euxanthone and diazobenzene-gentisin are devoid of tinctorial property, for when applied, in the form of finely divided pastes, to wool alone or mordanted with chromium, the patterns are hardly even stained during this process. This is interesting, for although gentisin and euxanthone are dyestuffs, and their original hydroxyls, as shown above, are intact in these compounds, their tinctorial effect has evidently been neutralised by the presence of the azobenzene group.

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LXX.—*The Vapour Pressures, Specific Volumes, and Critical Constants of Normal Heptane.*

By SYDNEY YOUNG, D.Sc., F.R.S., University College, Bristol.

IN previous papers (Trans., 1897, 71, 446; 1895, 67, 1071), the vapour pressures, specific volumes, and critical constants of normal pentane and normal hexane have been given, and it has been pointed out that, whilst the generalisations of Van der Waals regarding "corresponding" pressures, temperatures, and volumes hold good for these substances with a near approach to accuracy, yet the small deviations appear to depend on the molecular weight. Naturally, however, it would be unsafe to generalise from experiments with only two members of a series, and the hope was expressed that it would be possible to obtain data for normal heptane and normal octane.

Dr. Thorpe has very kindly placed his well-known specimen of normal heptane from *Pinus sabiniana* at my disposal, and I am now able to give the data for this paraffin. It will be seen that they are in agreement with the conclusions previously arrived at.

The boiling point of normal heptane is  $98\cdot43^{\circ}$ , and the sp. gr. at  $0^{\circ}$  is  $0\cdot70048$  (Thorpe, Trans., 1880, 37, 213).

*Vapour Pressures at Low Temperatures.*

The method of Ramsay and Young was employed for pressures up to 160 mm.; for higher pressures up to that of the atmosphere a modified distillation bulb with reflux condenser was used.

Press.	Temp.	Press.	Temp.	Press.	Temp.	Press.	Temp.
9.2	$-3\cdot4^{\circ}$	46.05	$25\cdot05^{\circ}$	153.8	$51\cdot95^{\circ}$	382.1	$76\cdot5^{\circ}$
10.6	$-1\cdot1$	57.35	$29\cdot65$	186.2	$56\cdot85$	431.2	$80\cdot2$
12.45	$+1\cdot2$	71.45	$34\cdot35$	205.2	$59\cdot4$	485.5	$83\cdot8$
15.3	$5\cdot0$	91.0	$40\cdot15$	229.6	$62\cdot35$	547.2	$87\cdot45$
18.15	$8\cdot05$	112.4	$44\cdot95$	257.7	$65\cdot55$	610.7	$91\cdot15$
22.65	$11\cdot7$	136.4	$49\cdot4$	294.3	$69\cdot2$	687.8	$95\cdot15$
28.95	$16\cdot1$	151.7	$51\cdot4$	334.4	$72\cdot65$	762.35	$98\cdot55$
36.15	$20\cdot35$						

The vapour pressures at high temperatures were determined with the pressure apparatus employed in previous researches, and the usual corrections were made.

The observed pressures (the mean of four readings in each case) together with those read from the curves constructed from the observations at low temperatures, and also the pressures calculated by means of Biot's formula

$$\log p = a + b \alpha^t + c \beta^t$$

are as follows.

The constants for Biot's formula are—

$$\begin{aligned} a &= 1.145148 \\ b &= 2.431040 & \log b &= 0.3857922 \\ c &= -2.517688 & \log c &= 0.4010018 \\ \log a &= 0.00053408 \\ \log \beta &= 1.99596377 \\ t &= t^\circ C. \end{aligned}$$

### *Vapour Pressures.*

Temperature.	Dynamical method from curve.	Statical method.	Calculated from Biot's formula.	Temperature.	Statical method.	Calculated from Biot's formula.
0°	11.45	—	11.45	150°	2784	2780.4
10	20.50	—	20.51	160	3450	2433.3
20	35.50	—	35.16	170	4212	4196.0
30	58.35	—	57.87	180	5091	5080.9
40	92.05	—	91.78	190	6095	6101.3
50	140.9	—	140.74	200	7261	7271.8
60	208.9	—	209.32	210	8594	8608.6
70	302.3	—	302.77	220	10105	10130
80	426.6	—	407.26	230	11810	11857
90	588.8	—	588.74	240	13790	13811
100	795.2	—	794.93	250	15980	16020
110	—	1047	1053.3	260	18470	18511
120	—	1367	1372.1	264	19610	19595
130	—	1753	1759.9	266.85	20430	20399
140	—	2229	2226.1	(Crit.)		

The critical temperature was taken to be 266.9°, and the critical pressure 20415 mm.

### *Volumes of a Gram of Liquid.*

These were determined in the pressure apparatus: up to 210° the volumes were read directly, but at higher temperatures they were calculated from observations of the volume of vapour, and the total volume of liquid and vapour by the method described in the Transactions (1893, 63, 1200).



The observed and smoothed specific volumes and the molecular volumes calculated from the smoothed specific volumes are given in the following table. From 0° to 100°, the smoothed values have been calculated from Thorpe's table of volumes of normal heptane— $V_0 = 1.00000$ —(*loc. cit.*).

The molecular weight is taken as 99.79.

*Volumes of a Gram and Molecular Volumes of Liquid.*

Tempera- ture.	Volumes of a gram.		Mole- cular volumes	Tempera- ture.	Volumes of a gram.		Mole- cular volumes
	Observed.	From curve.			Observed.	From curve.	
0°	—	1.4276	142.46	170°	1.8669	1.8660	186.21
10	—	1.4450	144.20	180	1.9126	1.9112	190.72
20	—	1.4629	145.98	190	1.9625	1.9620	195.79
30	1.4804	1.4813	147.82	200	2.0192	2.0195	201.53
40	1.5000	1.5003	149.72	210	2.0867	2.0865	208.21
50	1.5204	1.5200	151.68	220	2.1670	2.1665	216.20
60	1.5417	1.5406	153.74	230	2.2650	2.2655	226.07
70	1.5613	1.5621	155.88	240	2.3940	2.3940	238.90
80	1.5856	1.5846	158.13	250	2.5730	2.5730	256.80
90	1.6081	1.6082	160.48	256	2.7290	2.7290	272.30
100	1.6327	1.6330	162.96	260	2.8950	2.8930	288.70
110	1.6591	1.6591	165.56	262	3.0010	3.0010	299.50
120	1.6888	1.6875	168.40	264	3.1590	3.1590	315.20
130	1.7176	1.7180	171.44	265	3.2690	3.2690	326.20
140	1.7516	1.7510	174.74	266	3.4400	3.4400	343.30
150	1.7863	1.7862	178.25	266.5	3.5480	3.5480	354.10
160	1.8236	1.8245	182.07	266.9 (Crit.)	—	4.266*	425.7*

\* By the method of Cailletet and Mathias.

*Volumes of a Gram of Saturated Vapour.*

Determinations were made with the pressure apparatus and by the sealed tube method (*Trans.*, 1891, 59, 37, and *Phil. Mag.*, 1895).

The results are given in the table below, also the volumes of a gram read from curves constructed by plotting the logarithms of the volumes against the temperatures. The molecular volumes calculated from the smoothed specific volumes are also given.

*Volumes of a Gram and Molecular Volumes of Saturated Vapour.*

Temperature.	Volumes of a gram.				Molecular volumes.
	Pressure apparatus.	Sealed tube method.		From curves.	
		I.	II.		
70°	—	—	697	697	69500
80	—	—	516	501	50000
90	—	—	381	370	36900
100	—	—	280	279	27800
110	—	—	212	213·1	21250
120	—	—	165	164·8	16450
130	—	—	128·8	129·0	12870
140	—	—	102·5	102·3	10210
150	—	—	81·8	81·8	8170
160	—	—	66·2	66·3	6620
170	—	54·8	53·9	54·1	5400
180	—	45·3	44·15	44·6	4450
190	—	36·9	—	36·8	3675
200	—	30·3	—	30·27	3020
210	—	25·0	—	24·97	2492
220	20·44	20·45	—	20·44	2040
230	16·66	16·66	—	16·66	1663
240	13·45	13·40	—	13·43	1340
250	10·60	10·53	—	10·57	1055
256	8·97	8·91	—	8·95	894
260	7·77	7·77	—	7·77	776
262	7·18	7·165	—	7·16	715
264	6·50	6·480	—	6·50	649
265	6·10	—	—	6·13	612
266	5·60	5·645	—	5·625	561
266·5	5·28	—	—	5·280	527
266·9 (Crit.)	—	—	—	4·266*	425·7*

\* By the method of Cailletet and Mathias.

The critical volume of a gram and molecular volume were calculated from the critical density, which was ascertained by the method of Cailletet and Mathias (*Compt. rend.*, 1886, 102, 1202; 1887, 104, 1563; 1892, 115, 35).

The densities of liquid and saturated vapour, the mean densities and those calculated from the formula

$$D_t = 0.3518 - 0.00044t$$

are given below.

Temperature.	Density.		Mean density.		
	Liquid.	Saturated vapour.	Observed.	Calculated.	$\Delta \times 10^4$
70°	0·6402	0·0014	0·3208	0·3210	-2
80	0·6311	0·0020	0·3165	0·3166	-1
90	0·6218	0·0027	0·3122	0·3122	0
100	0·6124	0·0036	0·3080	0·3078	+2
110	0·6027	0·0047	0·3037	0·3034	+3
120	0·5926	0·0061	0·2993	0·2990	+3
130	0·5821	0·0078	0·2949	0·2946	+3
140	0·5711	0·0098	0·2904	0·2902	+2
150	0·5598	0·0122	0·2860	0·2858	+2
160	0·5481	0·0151	0·2816	0·2814	+2
170	0·5359	0·0185	0·2772	0·2770	+2
180	0·5232	0·0224	0·2728	0·2726	+2
190	0·5096	0·0272	0·2684	0·2682	+2
200	0·4952	0·0330	0·2641	0·2638	+3
210	0·4793	0·0401	0·2597	0·2594	+3
220	0·4616	0·0489	0·2552	0·2550	+2
230	0·4414	0·0600	0·2507	0·2506	+1
240	0·4177	0·0745	0·2461	0·2462	-1
250	0·3877	0·0946	0·2416	0·2418	-2
256	0·3664	0·1117	0·2390	0·2392	-2
260	0·3457	0·1287	0·2372	0·2374	-2
262	0·3332	0·1396	0·2364	0·2365	-1
264	0·3166	0·1538	0·2352	0·2356	-4
265	0·3059	0·1631	0·2345	0·2352	-7
266	0·2907	0·1778	0·2342	0·2348	-6
266·5	0·2819	0·1895	0·2357	0·2345	+12
266·9	—	—	—	0·2344	—

The critical constants are thus found to be—

Temperature 266·9°.

Pressure 20415 mm.

Density 0·2344. Volume of a gram 4·266 c.c.

Molecular volume 425·7.

It is noticeable that the critical densities of the four paraffins so far investigated are nearly identical; they are

Isopentane .....	0·2344
Normal pentane.....	0·2324
Normal hexane .....	0·2343
Normal heptane .....	0·2344

The absolute temperatures and the molecular volumes of liquid and saturated vapour were read from the curves at a series of pressures "corresponding" with those given in previous papers: from these data the ratios of the temperatures and volumes to the critical constants were calculated, also the ratios of the actual to the theoretical densities of saturated vapour.

Ratio of pressure to critical pressure.	Pressure.	Absolute temperature.	Molecular volume.		Abs. temp. Abs. crit. temp.	Vol. liq. Crit. vol.	Vol. sat. vap. Crit. vol.	Density sat. vap. Theor. density.
			Liquid.	Saturated vapour.				
0.001474	30.1	290.0°	145.44	—	0.5371°	0.3416	—	—
0.002949	60.2	303.7	147.94	—	0.5625	0.3475	—	—
0.005898	120.4	319.2	150.94	—	0.5912	0.3545	—	—
0.011795	240.8	336.75	154.58	—	0.6237	0.3631	—	—
0.022411	457.5	355.2	158.68	46700	0.6579	0.3727	109.6	1.033
0.044232	903.0	377.25	164.02	24780	0.6987	0.3853	58.2	1.048
0.088465	1806	404.0	171.78	12580	0.7483	0.4035	29.5	1.105
0.14744	3010	426.75	179.62	7570	0.7904	0.4219	17.8	1.164
0.20642	4214	443.0	186.21	5403	0.8205	0.4374	12.7	1.209
0.29488	6020	462.15	195.29	3729	0.8560	0.4587	8.76	1.279
0.44232	9030	485.85	210.36	2353	0.8999	0.4941	5.53	1.421
0.58978	12040	504.0	227.17	1626	0.9335	0.5336	3.82	1.600
0.73721	15050	518.75	248.18	1172	0.9608	0.5830	2.75	1.827
0.82568	16860	526.5	265.25	964	0.9752	0.6230	2.26	2.013
0.88465	18060	531.3	280.91	827	0.9841	0.6598	1.95	2.210
0.94363	19260	535.75	304.76	691	0.9923	0.7159	1.62	2.500
0.97313	19870	537.95	325.51	614	0.9964	0.7646	1.44	2.741
1.00000	20415	539.9	425.7	425.7	1.0000	1.0000	1.00	3.860

The influence of the molecular weight of the normal paraffins will be fully discussed when the data for normal octane have been obtained; meanwhile, it may be pointed out that, as with the ethereal salts, the ratios of the absolute temperatures (boiling points) at corresponding pressures to the absolute critical temperatures show a small but decided increase with rise of molecular weight. No definite relation between the volume ratios and the molecular weights of the ethereal salts could be traced, but in the case of the three normal paraffins so far studied, it appears that the ratios of the volumes of saturated vapour to the critical volumes, and of the actual to the theoretical critical densities, also increase with rise of molecular weight, whilst the ratios of the volume of liquid to the critical volume diminish slightly.

In the table below are given the ratios of the actual to the theoretical densities at the critical points and the other ratios at a single "reduced" pressure.

	Normal pentane.	Normal hexane.	Normal heptane.
<u>Actual critical density.</u> Theoretical critical density.	3.765	3.827	3.860

*Ratio of Pressure to Critical Pressure = 0.14744.*

<u>Absolute temperature.</u>	0.7769	0.7831	0.7904
<u>Absolute critical temperature.</u>			
<u>Volume of liquid.</u>	0.4245	0.4234	0.4219
<u>Critical volume.</u>			
<u>Volume of saturated vapour.</u>	17.0	17.6	17.8
<u>Critical volume.</u>			

## LXXI.—*Contributions to the Chemistry of Phenol Derivatives.\**

By RAPHAEL MELDOLA, F.R.S., and FREDERICK HENRY STREATFIELD.

### *Bromination and Nitration of Phenol.*

THERE is some discrepancy between the statements of different authors respecting the action of bromine on phenol. Hübner and Brenken (*Ber.*, 1873, 6, 170), by brominating phenol in acetic acid solution, obtained a solid (para) bromophenol, and stated that a "liquid isomeride" remained in the mother liquor after freezing out the solid modification. More recently, Gordon (*Proc.*, 1891, p. 64), repeating the experiment of Hübner and Brenken, came to the conclusion that the product was "practically pure parabromophenol." In a paper published by one of us with Messrs. Woolcott and Wray in 1896 (*Trans.*, p. 1326), it was stated that the bromination of phenol in glacial acetic acid gave a mixture of the para- and ortho-derivatives. The latter statement was based on indirect evidence derived from the study of the nitration of the crude product of the action of bromine on phenol, under the conditions specified. Among the bromonitrophenols thus formed there was always obtained a quantity of 2-bromo-4:6-dinitrophenol which seemed too great to be accounted for by isomeric change (Armstrong, *J. Chem. Soc.*, 1875, 520) under the conditions of nitration employed by us.

As the details of bromination and nitration were not given in the paper published in 1896, and as we have now obtained direct evidence of the presence of orthobromophenol in the product of bromination, it may be of interest to supply these details, as we are not sure whether our conditions of working were the same as either those of Hübner and Brenken or of Gordon. The phenol is dissolved in about its own weight of glacial acetic acid, and the calculated quantity of bromine

\* For the first instalment, see *Trans.*, 1896, 69, 1321.



dissolved in the same solvent (1 c.c. containing about 1.5 grams of bromine), allowed to fall, drop by drop, into the phenol solution, kept cold by immersion in water. The temperature during this operation does not exceed  $21^{\circ}$ . After all the bromine has been added, the solution is diluted with water, the oil which separates is washed repeatedly with water, and without further purification dissolved in about an equal volume of glacial acetic acid. The nitration is carried out in precisely the same way as the bromination, the calculated quantity of fuming nitric acid (sp. gr. 1.5), diluted with about three times its volume of acetic acid, being mixed gradually with the cooled solution of the bromophenols. The process of mixing takes about 2 hours, and the temperature does not exceed  $22^{\circ}$ . When about one-half the required quantity of nitric acid has been added, the solution begins to deposit crystals, and soon becomes semi-solid. The best method of treating the product was only discovered after a numerous series of operations with different lots of 50 or 100 grams of phenol, and the process now described may be considered as a summary of our experience.

After the completion of the nitration, the whole product is mixed with water, collected, washed until free from acid, and transferred to a flask with water. At this stage, three chief products are always present: (a) 4-bromo-2-nitrophenol predominating, (b) 2-bromo-4:6-dinitrophenol, (c) 2-bromo-4-nitrophenol. With respect to the origin of these products, we refer to the following portion of the paper. In order to separate them, the contents of the flask are steam distilled as long as anything comes over, the 4-bromo-2-nitrophenol being thus removed.\* The residue in the flask is treated with ammonia in excess, so as to convert the bromonitro-compounds into ammonium salts, and when quite cold filtered, so as to remove the 2-bromo-4:6-dinitrophenol ammonium salt, which is but slightly soluble in cold water; the filtrate now contains the whole of the 2-bromo-4-nitrophenol and a certain quantity of the bromodinitrophenol. On acidifying with hydrochloric acid, the latter separates after stirring for a short time, and can be removed by filtration, whilst the filtrate containing the more soluble bromonitrophenol is reduced by evaporation and allowed to stand, when the latter compound separates in flat, white needles melting at  $112^{\circ}$ . This bromonitrophenol is identical with that obtained by Brunck (*Zeit. f. Ch.*, 1867, 204) and by Körner (*ibid.*, 1868, 323), but these authors, who obtained the compound by brominating paranitrophenol, assign to it a melting point of  $102^{\circ}$ ; this discrepancy may be

\* The bromodinitrophenol is very slightly volatile in steam, but to a quite inappreciable extent, and can be recognised at once by its remaining solid in the condenser when the temperature is allowed to rise by running off the cold water. When this stage is reached the distillation is stopped.

due to a misprint, or to a difference in the degree of purity of the product obtained by us, or, again, to the use of water as a solvent. We have satisfied ourselves that the products are identical, by a comparison and analysis of the barium salts. We may add that the relatively high degree of solubility of this bromonitrophenol in water was only discovered after we had familiarised ourselves with its properties by obtaining it pure from another source, namely, by the nitration of orthobromophenol, as will be explained subsequently.

The origin of the three products above referred to was determined by a series of experiments with pure para- and ortho-bromophenols. The mixture obtained by the direct bromination of phenol contains, not only ortho- and para-bromophenols, but always a certain quantity of unbrominated phenol and a certain quantity of 2:4-dibromophenol, the formation of which it is impossible to avoid, under the conditions of bromination described. We have not found it possible to separate these bromo-derivatives directly from the mixture, but if the whole product is methylated by heating with the necessary quantities of potassium hydroxide and methylic iodide in methyl alcohol solution, the bromoanisoles thus obtained can be fractionally distilled. The monobromanisoles come over first, and the temperature then rises rapidly to  $272^{\circ}$ , the boiling point of 2:4-dibromanisol; the latter has a melting of  $59^{\circ}$ , as described by Körner. In the preparation of parabromophenol by the freezing out method of Hübner and Brenken, the other products are presumably contained in the mother liquor. The boiling points of ortho- ( $210^{\circ}$ ) and parabromanisol ( $223^{\circ}$ ) are too near to admit of satisfactory separation by fractional distillation without a large supply of material.

#### *Nitration of Parabromophenol.*

Pure parabromophenol was prepared by two methods, independently of the direct bromination of phenol. Parabromosalicylic acid, prepared by the bromination of salicylic acid, and subsequent purification of the product, was distilled with dry barium carbonate according to Cahours' method (*Annalen*, 52, 338); another preparation was made from pure parabromaniline by the diazo-method. These preparations were nitrated in acetic acid solution, as before, only in the latter case the nitration was carried on in a freezing mixture. Both preparations gave the same products, namely, 4-bromo-2-nitrophenol and a small quantity of 2-bromo-4:6-dinitrophenol; in these cases, therefore, the latter compound is undoubtedly produced by intramolecular change, since no orthobromophenol was present, and this accounts for the production of a portion of this bromodinitrophenol during the nitration of the mixture obtained by the direct bromination of phenol. It

is remarkable that this change should occur at the low temperature at which the nitration was effected, since no excess of nitric acid was used, and previous observers (Armstrong and Gordon) have always brought about the transformation by heating 4-bromo-2:6-dinitrophenol with bromine water or nitric acid. It has recently been shown by Reverdin (*Ber.*, 1896, 29, 997, 2595; 1897, 30, 2999) that a somewhat similar transference of iodine from the para- to the ortho-position takes place on nitrating periodoanisole, &c., but this observation is not really parallel to the present case, as will be made evident from the experiments described subsequently.

A specimen of parabromophenol purchased from Schuchardt gave the same results as our own preparations; from this specimen we also obtained a small quantity of 2-bromo-4-nitrophenol in addition to the other products, thus indicating the presence of orthobromophenol. The crystals of this specimen were, however, wet with the acetic acid mother liquor, from which they had been only imperfectly drained, so the remainder was steam distilled to bring over any orthobromophenol; the residue, on nitration, then give only the 4-bromo-2-nitro- and the 2-bromo-4:6-dinitrophenol, and not a trace of the 2-bromo-4-nitrophenol. This experiment shows that the latter compound results from the nitration of orthobromophenol, and thus proves the presence of this modification in the product of the direct bromination of phenol; at the same time, the fact that pure parabromophenol does not give 2-bromo-4-nitrophenol on nitration shows that there is no analogy between this compound and the iodine derivatives nitrated by Reverdin under the conditions of nitration employed by us. This author shows, in fact (*Ber.*, 1896, 29, 2598), that parabromanisole can be nitrated without a shifting of the bromine atom.

Direct evidence of the existence of orthobromophenol in the product of the bromination of phenol in acetic acid was obtained by following Hübner and Brenken's method; two distinct experiments were made, the bromine solution in each case being dropped slowly into the acetic acid solution of the phenol cooled in melting ice. The temperature during this operation keeps at 2—3°. In one case, the solution, after bromination, was warmed so as to drive off hydrogen bromide, but this does not appear to influence the product in any way beyond giving a slightly better yield of parabromophenol. In both experiments, after bromination, the parabromophenol was frozen out by immersing the beaker containing the solution in ice and salt and stirring the contents; the crystalline pulp was then collected, drained, and allowed to dry in the air, and finally purified by crystallisation from chloroform. The acetic acid mother liquor was diluted with water and the oily layer separated. The two products, consisting of (1) pure parabromophenol, and (2) an oily mixture of para- and ortho-

bromophenols, were then nitrated separately in acetic acid under the same conditions as described above, equal weights being taken so as to make the results comparable. From the parabromophenol there was obtained only 4-bromo-2-nitrophenol, and some of the 2-bromo-4:6-dinitrophenol. From the oily mixture there was obtained in addition some 2-bromo-4-nitrophenol, which was identified by its melting point, and a nitrogen determination.

0.1826 gave 9.8 c.c. moist nitrogen at 17° and 759 mm.  $N = 6.20$ .  
 $C_6H_3Br \cdot NO_2 \cdot OH$  requires  $N = 6.42$  per cent.

*Nitration of Orthobromophenol.*

Orthobromophenol was prepared from orthonitrophenol by reducing the latter to amidophenol with ammonium sulphide and replacing the  $NH_2$ -group by bromine by Sandmeyer's method; the bromophenol is very readily distillable in a current of steam, and comes over as a colourless oil, having a marked and peculiar odour, which can be recognised in the product obtained by the direct bromination of phenol. The nitration was carried out in acetic acid solution as before, with the calculated quantity (1 mol.) of nitric acid (1.5 sp. gr.), cooling being effected by simply immersing the beaker containing the solution in cold water. The product on mixing with water sinks as a dark coloured oil, which does not solidify on standing for many days; it was found to consist of two bromonitrophenols, the 2-bromo-4-nitro-modification of Brunck and Körner melting at 112°, and a new modification which comes over readily on steam distillation. The 2:4-modification was identified with Brunck and Körner's compound by analysing the barium salt, which consists of orange-yellow needles having the composition  $(NO_2 \cdot C_6H_3Br \cdot O)_2Ba + 6H_2O$ .

0.620, dried under desiccator, gave 0.0549  $BaSO_4$ .  $Ba = 19.99$ .

0.3217, dried at 160—170° until constant, lost 0.0517.  $H_2O = 16.07$ . The formula requires  $Ba = 20.17$  per cent. and  $H_2O = 15.90$  per cent.\*

The new modification which comes over on steam distillation crystallises from dilute alcohol in pale yellow needles having a melting point of 67—68°.

0.20 gave 11 c.c. moist nitrogen at 13.5° and 746 mm.  $N = 6.34$ .

$C_6H_3Br(NO_2) \cdot OH$  requires  $N = 6.42$  per cent.

The barium salt forms flat, reddish-yellow needles sparingly soluble in hot water.

\* We have found that, under certain conditions, this bromonitrophenol can also form a hydrate containing  $7H_2O$ .

0.9146, dried at 160—170° until constant, lost 0.1650.  $H_2O = 18.04$ . The formula requires  $H_2O = 18.07$  per cent.



0.1560, dried under desiccator, gave 0.0596  $\text{BaSO}_4$ .  $\text{Ba} = 22.46$ .

0.2328, dried under desiccator and then heated at  $170^\circ$ , lost 0.0136  $\text{H}_2\text{O} = 5.84$ .  
 $(\text{NO}_2 \cdot \text{C}_6\text{H}_3\text{Br} \cdot \text{O})_2\text{Ba} + 2\text{H}_2\text{O}$  requires  $\text{Ba} = 22.57$  and  $\text{H}_2\text{O} = 5.93$  per cent.

The potassium salt is readily soluble in hot water and crystallises from this solvent in ruby-coloured needles.

0.1544, dried under desiccator, gave 0.0492  $\text{K}_2\text{SO}_4$ .  $\text{K} = 14.28$ .

0.1612, dried under desiccator and subsequently at  $100^\circ$ , lost 0.011  $\text{H}_2\text{O} = 6.82$ .

$\text{NO}_2 \cdot \text{C}_6\text{H}_3\text{Br} \cdot \text{OK} + \text{H}_2\text{O}$  requires  $\text{K} = 14.23$  and  $\text{H}_2\text{O} = 6.56$  per cent.

0.1438, dried at  $100^\circ$ , gave 0.0494  $\text{K}_2\text{SO}_4$ .  $\text{K} = 15.39$ .

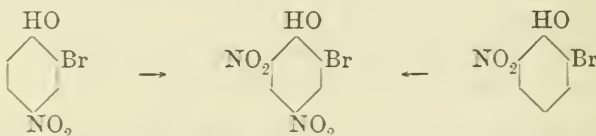
$\text{NO}_2 \cdot \text{C}_6\text{H}_3\text{Br} \cdot \text{OK}$  requires  $\text{K} = 15.23$  per cent.

The silver salt, which was prepared for the purpose of obtaining the methylic ether, crystallises in ochreous needles fairly soluble in boiling water, but only sparingly in cold water. On heating with methylic iodide in methyl alcohol in a flask with a reflux condenser for some hours, the silver salt is decomposed and the methylic ether formed. The latter, purified by crystallisation from dilute alcohol, forms white, silvery scales melting at  $67^\circ$ .

0.0940 gave 4.75 c.c. moist nitrogen at  $15.4^\circ$  and 766.5 mm.  $\text{N} = 5.94$ .

$\text{NO}_2 \cdot \text{C}_6\text{H}_3\text{Br} \cdot \text{OCH}_3$  requires  $\text{N} = 6.03$  per cent.

The constitution of the new bromonitrophenol is shown by its giving 2-bromo-4:6-dinitrophenol on further nitration, 2-bromo-4-nitrophenol giving the same dinitro-compound on further nitration. The new modification is thus 2-bromo-6-nitrophenol.



*2-Bromo-6-nitraniline*.—This compound, obtained by heating the methylic ether, above described with alcoholic ammonia in a sealed tube at  $120^\circ$  for 7 hours, crystallised from dilute alcohol in silky, orange needles melting at  $73-74^\circ$ .

0.1269 gave 13.9 c.c. moist nitrogen at  $12^\circ$  and 767 mm.  $\text{N} = 13.10$ .

$\text{NO}_2 \cdot \text{C}_6\text{H}_3\text{Br} \cdot \text{NH}_2$  requires  $\text{N} = 12.90$  per cent.

The compound is soluble in all the ordinary organic solvents; it is but very feebly basic and resists acetylation even when boiled with acetic anhydride.

From the foregoing results, it thus appears that the 2-bromo-4:6-dinitrophenol, obtained by the nitration of the crude product of the action of bromine on phenol in acetic acid solution, owes its



origin to both the para- and ortho-bromophenols present in the mixture. Its formation from parabromophenol under the conditions of nitration employed is certainly remarkable, and since at first sight it appeared probable that the dinitro-compound resulted from the further nitration of 4-bromo-2-nitrophenol (with isomeric change), a number of experiments were made with the object of studying the action of nitric acid on the latter compound under various conditions. The results are summarised below.

(a) 4-Bromo-2-nitrophenol may be dissolved in excess of cold fuming nitric acid without transformation into 2-bromo-4:6-dinitrophenol, provided the temperature is not allowed to rise above  $20^{\circ}$ , and the action of the nitric acid is not allowed to continue for more than about 5 minutes. The product is 4-bromo-2:6-dinitrophenol.

(b) 4-Bromo-2-nitrophenol is not converted into 2-bromo-4:6-dinitrophenol by a large excess (ten times the theoretical quantity) of fuming nitric acid in 2—3 hours if the nitric acid is diluted with an equal volume of glacial acetic acid, and the temperature not allowed to exceed  $15^{\circ}$ . The product in this case also is 4-bromo-2:6-dinitrophenol.

(c) 4-Bromo-2-nitrophenol is completely converted into 2-bromo-4:6-dinitrophenol at ordinary temperatures if dissolved in excess of fuming nitric acid and allowed to stand for 2 or 3 hours.

The formation of 2-bromo-4:6-dinitrophenol thus appears to be due to the direct action of nitric acid on parabromophenol (and ortho-bromophenol), the para-modification not passing through the intermediate stage of 4-bromo-2-nitrophenol.

#### *4-Bromo-2:6-dinitrophenol and Derivatives.*

The above compound can be reduced by heating with ammonium sulphide solution. An excess of the reducing agent must be avoided or the reduction goes too far, and a highly oxidisable compound is formed. The product of the moderated reduction is 4-bromo-2-nitro-6-amidophenol. When crystallised from dilute alcohol, the compound consists of brown scales of distinctly basic properties melting at  $141-142^{\circ}$ .

0.1862 gave 19.1 c.c. moist nitrogen at  $9.5^{\circ}$  and 753.4 mm.  $N = 12.18$ .

$\text{NO}_2 \cdot \text{C}_6\text{H}_2\text{Br}(\text{NH}_2) \cdot \text{OH}$  requires  $N = 12.01$  per cent.

The acetyl derivative,  $\text{NO}_2 \cdot \text{C}_6\text{H}_2\text{Br}(\text{NHAc}) \cdot \text{OH}$ , prepared by acetylating the base with acetic anhydride in acetic acid solution, after crystallisation from alcohol, acetic acid, and benzene successively, consists of whitish needles melting at  $161-162^{\circ}$ .

0.0949 gave 8.3 c.c. moist nitrogen at  $15.2^{\circ}$  and 759.5 mm.  $N = 10.3$ .

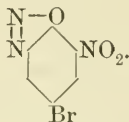
The formula requires  $N = 10.18$  per cent.

The hydrochloric acid solution of the base, when treated with one molecular proportion of sodium nitrite, gives a brownish-yellow crystalline deposit of a diazoxide which, when dry, crystallises from benzene in brown, stumpy needles with a greenish, metallic lustre. The pure compound when heated rapidly, explodes with extreme violence at about  $144^{\circ}$ . The composition was established by analysis.

0.2166 gave 31.5 c.c. moist nitrogen at  $13^{\circ}$  and 762 mm.  $N = 17.1$ .

The formula requires  $N = 17.2$  per cent.

The constitution is



In order to characterise the bromodinitrophenol further, the methylic ether, which does not appear to have been described, was prepared by heating the silver salt with methylic iodide in methyl alcoholic solution. The methylation is very imperfect, and the product, after purification by washing with dilute alkali and crystallisation from dilute alcohol, consists of slender, straw-coloured needles melting at  $81-82^{\circ}$ .

0.0783 gave 6.8 c.c. moist nitrogen at  $20^{\circ}$  and 764 mm.  $N = 9.97$ .

$C_6H_2Br(NO_2)_2 \cdot OCH_3$  requires  $N = 10.10$  per cent.

This methylic ether most readily exchanges its methoxyl group for the amido-group on boiling for a short time with alcoholic ammonia, the product being the 4-bromo-2:6-dinitraniline crystallising in orange needles melting at  $160^{\circ}$  (Austen, *Ber.*, 1886, 9, 919).

0.0770 gave 10.9 c.c. moist nitrogen at  $19^{\circ}$  and 763 mm.  $N = 15.98$ .

$C_6H_2Br(NO_2)_2 \cdot NH_2$  requires  $N = 16$  per cent.

The protecting influence of the two orthonitro-groups is shown by the fact that the compound is not acetylated on boiling for some time with acetic anhydride and anhydrous sodium acetate. On boiling with benzoyl chloride, it forms a benzoyl derivative which crystallises from alcohol in white, silky needles melting at  $197-198^{\circ}$ .

0.0578 gave 5.7 c.c. moist nitrogen at  $19.5^{\circ}$  and 769.8 mm.  $N = 11.44$ .

$C_6H_2Br(NO_2)_2 \cdot NH \cdot C_7H_5O$  requires  $N = 11.47$  per cent.

#### *Derivatives of Guaiacol.*

*Bromonitroguaiacols.*—The origin of this experiment was an attempt to isolate a definite monobromoguaiacol by brominating guaiacol in glacial acetic acid with one molecular proportion of bromine, and the

conversion of the whole product into the benzoyl derivative by treatment with benzoyl chloride in the presence of caustic soda solution. The mixture of bromoguaiacol benzoates obtained by this method is, however, not crystallisable, and nitration was therefore resorted to as a means of isolating a definite compound. The product, consisting of a viscid, fragrant resin, was dissolved in glacial acetic acid, and allowed to stand for some hours in admixture with an excess of fuming nitric acid at the ordinary temperature. The nitro-derivative was thrown out by pouring the solution into water, and, after numerous crystallisations from alcohol, a definite compound consisting of slender pale-yellow needles, melting at  $103\text{--}104^\circ$ , was obtained.

0.120 gave 4.15 c.c. moist nitrogen at  $15.5^\circ$  and 745.5 mm.  $N = 3.95$ .

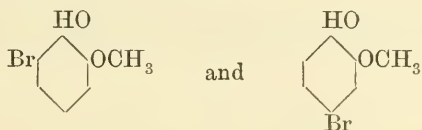
$\text{NO}_2 \cdot \text{C}_6\text{H}_2\text{Br}(\text{OCH}_3) \cdot \text{OC}_7\text{H}_5\text{O}$  requires  $N = 3.98$  per cent.

The benzoyl derivative was hydrolysed by boiling it for some time with sodium hydroxide solution; the sodium salt of the bromonitroguaiacol thus formed crystallises in bright red needles readily soluble in hot water, but only sparingly in cold water, especially in the presence of excess of sodium hydroxide. The free compound obtained by the action of acids on the sodium salt, crystallises from hot water in pale yellow plates or flat needles having a melting point of  $120^\circ$ .

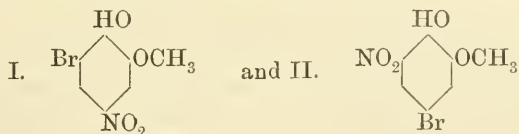
0.1426 gave 6.9 c.c. moist nitrogen at  $18^\circ$ , and 763 mm.  $N = 5.60$ .

$\text{NO}_2 \cdot \text{C}_6\text{H}_2\text{Br}(\text{OCH}_3) \cdot \text{OH}$  requires  $N = 5.64$  per cent.

The constitution of this bromonitroguaiacol has been arrived at indirectly. The bromination of guaiacol might be expected to give rise to a mixture of the two compounds



These, on nitration, would yield respectively



It was found that the paranitroguaiacol corresponding with formula I (Meldola, Proc., 1896, p. 127), on bromination in acetic acid, gave a bromonitroguaiacol differing from formula I, so that the bromonitroguaiacol melting at  $120^\circ$  isolated by us is the 4-bromo-6-nitroguaiacol (formula II). The deep red colour of the sodium salt is also in favour of this formula.

The 4-nitro-6-bromoguaiacol (formula I) obtained by brominating paranitroguaiacol, crystallises from hot water in pale, slender, yellow needles melting at  $142^{\circ}$ .

0.1320 gave 6.1 c.c. moist nitrogen at  $141^{\circ}$  and 769.5 mm.  $N = 5.49$ .

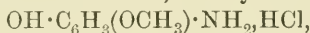
The formula requires  $N = 5.64$  per cent.

The sodium salt, which is much more soluble in water than that of the isomeride, crystallises in reddish needles, which are not so highly coloured as the sodium salt of the 4-bromo-6-nitroguaiacol.

The benzoyl derivative crystallises from benzene in thin, pale yellow tablets melting at  $117-118^{\circ}$ .

The bromamidoguaiacol, corresponding with the two bromonitroguaiacols above described, appear to be very easily oxidisable, and we have not yet succeeded in isolating them.

*Orthacetamidoguaiacol*.—The orthonitroguaiacol benzoate melting at  $88-89^{\circ}$  (Proc., 1896, p. 127), when reduced by boiling in alcohol solution with tin and hydrochloric acid, loses the benzoyl group and gives orthamidoguaiacol. The latter is very unstable, and could not be isolated as a free base; the hydrochloride,

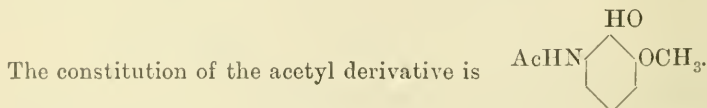


crystallises in white needles. The acetyl derivative, obtained by heating the hydrochloride with sodium acetate and acetic anhydride, crystallises from boiling water in flat, whitish needles with serrated edges, and melts at  $122-123^{\circ}$  with decomposition.

0.1396 (dried in air) gave 8.05 c.c. moist nitrogen at  $12^{\circ}$  and 767 mm.  $N = 6.9$ .

0.6927, dried at  $100^{\circ}$  until constant, lost 0.0678.  $\text{H}_2\text{O} = 9.78$ .

$\text{OH} \cdot \text{C}_6\text{H}_3(\text{OCH}_3) \cdot \text{NH} \cdot \text{C}_2\text{H}_5\text{O} + \text{H}_2\text{O}$  requires  $N = 7.03$  and  $\text{H}_2\text{O} = 9.04$  per cent.



The compound is phenolic, and forms a nitroso-derivative when dissolved in glacial acetic acid and treated with sodium nitrite. This nitroso-derivative crystallises in reddish-brown crystals having a melting point of about  $155^{\circ}$ , but the quantity of substance at our disposal was extremely small, and we do not consider that it has yet been obtained in a pure condition.

We have pleasure in acknowledging the assistance which Mr. Percy P. Phillips has given in connection with some of these investigations.

FINSBURY TECHNICAL COLLEGE,  
July, 1898.

LXXII.—*Some Iodoso-compounds.*

By JOHN MCCRAE, Ph.D.

IN order to ascertain whether diortho-substituted phenylic iodides yield iododichloride-, iodoso-, and iodoxy-derivatives, the following investigation was carried out.

Victor Meyer and others have shown that diortho-substituted benzoic acids do not yield ethereal salts by the hydrochloric acid method, and as this has been attributed by Meyer to the "surrounding" influence of the ortho-substituting groups, it was thought that the "surrounding" influence of two ortho-substituting groups might prevent the adding on of chlorine to the iodine. The results obtained have not confirmed this view, but the substances obtained are worthy of being recorded.

I. *Orthiododimetadibromotoluene*,  $C_6H_2(CH_3)IBr_2$  [1 : 2 : 3 : 5].

This substance has not yet been described. It was prepared by diazotising 3 : 5-dibromorthotoluidine\* in sulphuric acid solution, pouring the diazo-solution into a hot concentrated solution of potassium iodide, and warming on the water bath, when a dark coloured oil separated. As, on cooling, the oil readily solidified, the liquid was poured off, the solid melted under hot water, and a current of sulphurous anhydride passed through, when it was quickly decolorised. After being several times crystallised from alcohol, long, colourless needles were obtained melting at  $68^\circ$ . It is easily soluble in hot alcohol, ether, or chloroform. It boils with slight decomposition at  $314^\circ$  (uncorr.), and is only very difficultly volatile in steam.

0.1505 gave 0.2466 mixed AgBr and AgI.

$C_7H_5Br_2I$  requires 0.2446.

0.2210 mixed silver halides gave 0.1570 AgCl.

$2AgBr + AgI$  requires 0.1558 AgCl.

*Dichloride*,  $CH_3 \cdot C_6H_2Br_2 \cdot ICl_2$ .—A current of dry chlorine was passed through a saturated chloroform solution of iododibromotoluene, kept cool by being surrounded by water, and after some time yellow, cubical crystals of the dichloride separated. As the dichloride is more soluble in chloroform than the substance from which it is prepared, it does not separate until some of the chloroform has evaporated. The crystals were collected on a filter, washed with a small amount of chloroform, and dried on porous porcelain. The compound is easily soluble in ether, somewhat soluble in chloroform, and less so in

\* Obtained by aspirating a current of air saturated with bromine vapour through a hydrochloric acid solution of orthotoluidine.



alcohol; it melts (but not very definitely) at about  $95^{\circ}$  with evolution of much gas.

The analysis was carried out by estimating the amount of iodine liberated from potassium iodide (operation carried out in acid solution in an opaque bottle) by means of standard thiosulphate solution.

0.5425 liberated 0.3046 iodine, which corresponds with 15.70 per cent. Cl.

$C_7H_5Br_2I \cdot Cl_2$  requires Cl = 15.88 per cent.

(The melting point of the residue in this and all the following analyses was taken, and always was found to be the same as that of the original substance—in this case  $68^{\circ}$ .)

*Iodosodibromotoluene*,  $CH_3 \cdot C_6H_2Br_2 \cdot IO$ .—The dichloride triturated in a mortar with soda solution until the solid was free from chlorine, gave a compound which was too poor in oxygen. Better results were obtained, however, when a fairly dilute solution of sodium carbonate was used. The compound, dried on porous porcelain after completely washing with water, was a yellow, amorphous powder with characteristic iodoso-odour. Analysis showed that it contained 2.84 per cent. oxygen (calc. 4.08 per cent.). It was washed with alcohol and then dried. The yellowish powder thus obtained had no sharp melting point, at  $77^{\circ}$  it sintered, and at  $87^{\circ}$  was completely melted with disengagement of gas; when quickly heated, it explodes. It is soluble in ether, and to some extent in alcohol.

0.2665 liberated 0.1689 of iodine. O = 4.00.

$C_7H_5Br_2IO$  requires O = 4.08 per cent.

In the filtrate from the iodoso-compound, the presence of an iodonium salt was recognised by precipitation with potassium iodide.

*Iodosodiacetate and Iodoxydibromotoluene*.—To the iodoso-compound dissolved in glacial acetic acid water was added until it became slightly turbid, and the liquid was kept in the exsiccator for two or three days, when it deposited needle-shaped crystals melting at  $66.5^{\circ}$ ; these, according to the analysis, have the composition  $CH_3 \cdot C_6H_2Br_2 \cdot I(C_2H_3O_2)_2$ .

The iodoxy-compound,  $CH_3 \cdot C_6H_2Br_2 \cdot IO_2$ , was obtained by distilling the iodoso-derivative in a current of steam. The undistilled liquid, on being filtered and allowed to cool, deposited leafy crystals which exploded when heated. The amount of substance obtained was not sufficient to carry out an analysis, but it liberates a large quantity of iodine from acidified potassium iodide solution.

## II. *Symmetrical tribromiodobenzene*, $C_6H_2Br_3I$ [1 : 3 : 5 : 2].

This was prepared by treating diazotised sym-tribromaniline with potassium iodide solution and purification of the product by crystallisation from alcohol. The melting point found was  $105.5^{\circ}$  (Silber-

stein, *J. pr. Chem.*, 1883, [ii], 27, 101, found  $103.5^\circ$ , Jackson and Calvert,  $104.5^\circ$ , *Amer. Chem. J.*, 1896, 18, 298).

*Dichloride of tribromiodobenzene*,  $C_6H_2Br_3 \cdot ICl_2$ , was prepared exactly as dibromiodotoluene dichloride. The crystals melt and decompose slightly below  $100^\circ$ . They are easily soluble in ether and somewhat soluble in chloroform.

0.2175 liberated 0.1064 iodine.  $Cl = 13.67$ .

$C_6H_2Br_3ICl_2$  requires  $Cl = 13.86$  per cent.

*Iodosotribromobenzene*,  $C_6H_2Br_3 \cdot IO$ .—Trituration of the dichloride in a mortar either with dilute or concentrated solutions of caustic soda or of sodium carbonate until the solid was free from chlorine, did not yield the pure iodoso-compound. This was obtained, however, from the product of treatment by sodium carbonate or caustic soda after it had been dried, by washing with not too large a quantity of 90 per cent. alcohol. After drying on porous porcelain, a yellow, amorphous powder was obtained, which explodes when heated in the flame. At  $112^\circ$  it sinters, and at  $145^\circ$  melts completely.

0.2285 liberated 0.1250 iodine.  $O = 3.45$ .

$C_6H_2Br_3IO$  requires  $O = 3.50$  per cent.

*Iodosodiacetate*,  $C_6H_2Br_3 \cdot I(C_2H_3O_2)_2$ , was obtained exactly as the diacetate formerly described. It forms small, needle-shaped crystals, which sinter at  $98^\circ$  and melt completely about  $137^\circ$ . It liberates iodine from potassium iodide, but no analysis was made.

*Iodoxytribromobenzene*,  $C_6H_2Br_3 \cdot IO_2$ , was obtained by distilling the iodoso-compound in steam. From the undistilled part, flaky crystals separated; these explode when heated, and melt at  $193^\circ$ . They liberate iodine in large quantity from potassium iodide.

### III. 5-Nitro-2-iodotoluene.

Under the impression that the compound melting at  $104^\circ$ , which Beilstein and Kühlberg (*Annalen*, 1871, 158, 347) obtained by nitration of ortho-iodotoluene might be diorthomethylnitrophenylic iodide, I had started the preparation of it in order to determine its constitution before the work of Réverdin (*Ber.*, 1897, 30, 2999) was published. Réverdin has shown that Beilstein and Kühlberg's compound has the constitution  $CH_3 \cdot C_6H_3I \cdot NO_2$  [1 : 2 : 5].

Starting with this compound, the dichloride, iodoso-, &c., derivatives have been prepared, and although this has no bearing on the original idea of the work, a description of the compounds may be given here.

*Dichloride*,  $CH_3 \cdot C_6H_3(NO_2) \cdot ICl_2$ , was obtained by passing dry chlorine through a saturated chloroform solution of nitroiodotoluene.

Yellow crystals soon separated out; they are soluble in ether and in chloroform, also in alcohol, and decompose with evolution of gas at  $102^{\circ}$ .

0.1777 liberated 0.13505 iodide.  $\text{Cl} = 21.24$ .

$\text{C}_7\text{H}_6\text{NO}_2\text{ICl}_2$  requires  $\text{Cl} = 21.25$  per cent.

*Iodoso-derivative*,  $\text{CH}_3 \cdot \text{C}_6\text{H}_3(\text{NO}_2) \cdot \text{IO}$ .—The dichloride was triturated in a mortar with excess of a 12 per cent. solution of caustic soda, and the solid collected, washed, and dried after it was free from chlorine. The yellowish, amorphous powder thus obtained melted about  $175^{\circ}$ , and was slightly soluble in alcohol.

0.0675 liberated 0.0607 iodine.  $\text{O} = 5.67$ .

$\text{C}_7\text{H}_6\text{NO}_2\text{IO}$  requires  $\text{O} = 5.73$  per cent.

*Iodoso-diacetate and dinitrate*.—The iodoso-compound yields a diacetate,  $\text{CH}_3 \cdot \text{C}_6\text{H}_3(\text{NO}_2)\text{I}(\text{C}_2\text{H}_3\text{O}_2)_2$ , by treatment with glacial acetic acid and precipitation with water; the long, colourless needles thus obtained melted at about  $135^{\circ}$ .

The iodoso-compound is soluble in warm dilute nitric acid, and from the solution, on cooling, small crystals separate; this is the dinitrate,  $\text{CH}_3 \cdot \text{C}_6\text{H}_3(\text{NO}_2)\text{I}(\text{NO}_3)_2$ . At  $104^{\circ}$  it becomes half melted, but only fuses completely at  $150^{\circ}$ , and then with evolution of much gas and a slight separation of iodine.

0.1085 liberated 0.07025 iodine.  $\text{NO}_3 = 31.61$ .

$\text{C}_7\text{H}_6\text{NO}_2\text{I}(\text{NO}_3)_2$  requires  $\text{NO}_3 = 31.95$  per cent.

*Iodoxy-compound*,  $\text{CH}_3 \cdot \text{C}_6\text{H}_3(\text{NO}_2) \cdot \text{IO}_2$ , was obtained by distilling the iodoso-compound with steam, and even by simply boiling it with water. The undistilled liquid, when filtered and allowed to cool, deposited thin, tabular crystals; these, when quickly heated, explode, but have a very sharp melting point,  $198^{\circ}$ .

*Iodonium Iodide*,\*  $(\text{CH}_3 \cdot \text{C}_6\text{H}_3 \cdot \text{NO}_2)_2\text{I} \cdot \text{I}$ .—In the preparation of the iodoso-compound, the alkaline filtrate was slightly yellow, and with potassium iodide gave a white, crystalline precipitate which melted at  $99^{\circ}$  when dry. In all probability this was dinitrotolylidonium iodide, as, when rubbed, it showed the characteristic electric property of the iodonium iodides of springing away from the glass rod.

The investigation was not carried farther, for enough had been done to show that the original supposition was not correct.

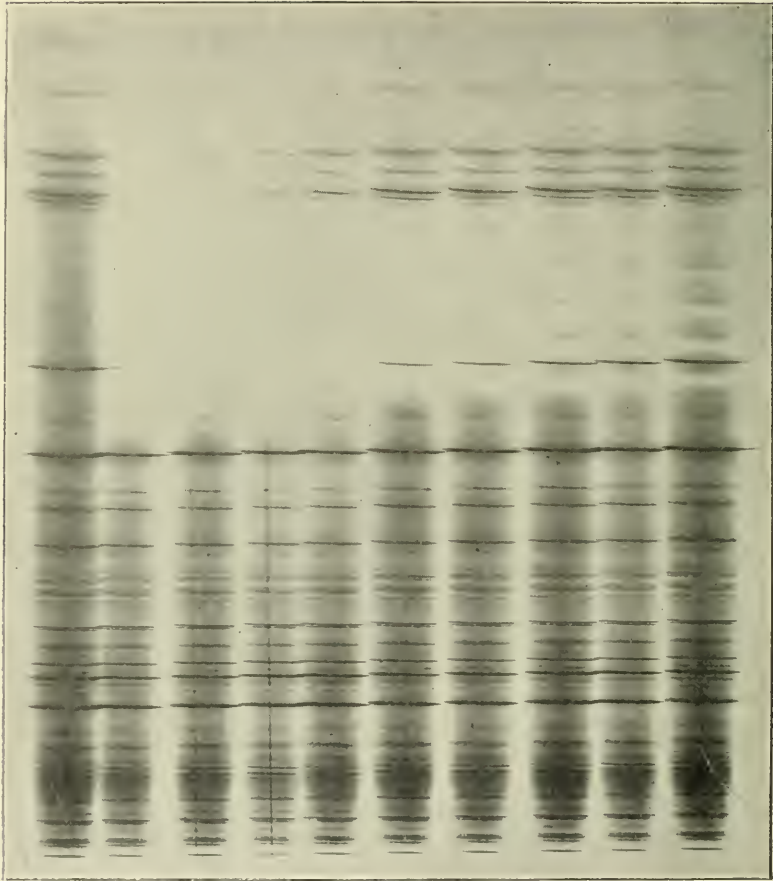
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LEEDS.

\* The theory of this formation is given in my Dissertation: Heidelberg, 1895.



*Benzene Absorption Bands.*

1 2 3 4 5 6





LXXIII.—*Notes on the Absorption-Bands in the Spectrum of Benzene.*

By W. N. HARTLEY, F.R.S. and J. J. DOBBIE, M.A., D.Sc.

In the earliest paper on the spectrum of benzene (Hartley and Huntington, *Phil. Trans.*, 1879, 170, 257), it was described as having six absorption bands, four of which are more persistent and stronger than the other two. Owing to the want of means to obtain a continuous spectrum, some difficulty was experienced in measuring with accuracy the weaker bands (Hartley, *Trans.*, 1885, 47, 685). By using a wide slit, long focussed lenses, and a powerful spark, the rays are sufficiently continuous, but at a sacrifice of accurate measurement of the fiducial spark lines. One feature, however, was noticeable in spectra obtained in this way, the absorption bands were all degraded in the direction of the least refrangible rays, or, in other words, towards the red end of the spectrum. This was considered as suggestive of the bands consisting of groups of lines stronger and closer together on the more refrangible side, weaker and wider apart on the less refrangible. By using a very powerful spark, the rays emitted by cadmium electrodes may be rendered sufficiently continuous to show these bands, and at the same time render the lines sufficiently sharp to measure them by; from such a photograph, taken a year ago, the absorption bands have been again measured.

The paper by Herr Pauer on the absorption of the ultra-violet rays by vapours and liquids (*Ann. Phys. Chem.*, 1897, 61, 362) shows that the spectrum of the vapour of benzene is composed of four absorption bands, similarly constituted of groups of lines. Liquid benzene does not show the constitution of these bands, neither do solutions of the hydrocarbon. Pauer also mentions a weaker band  $\lambda 239$  to  $236$  and indicates a line at  $\lambda 267$  which is weak. This last line is undoubtedly the 1st absorption band and the band  $\lambda 239$  to  $236$  is the 6th absorption band observed in solutions of benzene in alcohol.

It has therefore been considered desirable that photographs of the benzene spectrum should be submitted to the Society, together with a later series of measurements taken from solutions of benzene in alcohol.

*Benzene*,  $C_6H_6$ .—0.078 gram, 1 milligram molecule, dissolved in 20 c.c. of alcohol. Strong absorption bands to the number of six, which appear after dilution, or in decreasing thickness of liquid when the general absorption has disappeared.

Thickness of layer of liquid in millimetres.	Description of spectrum.	$\frac{1}{\lambda}$	$\lambda$
25	One band, absorption beyond complete	3691—3727	2709—2683
20	One band .....	3691—3727	2709—2683
	Rays feebly transmitted from 3727 to	3741	2673
	The strong lines of cadmium are feebly transmitted, viz., $\frac{1}{\lambda}$ 4306, 4321, 4368 and 4413.		
15	The same, but the transmitted lines are a little stronger.		
10	Two bands, not very distinct.		
	First from .....	3691—3730	2709—2681
	Second from .....	3755—3883	2663—2575
	Lines of cadmium transmitted more strongly 4291 to .....	4555	2195
5	The first absorption band is barely visible.		
	The second absorption band from ...	3802—3854	2630—2594
	Rays transmitted from 3854 to .....	3886	2573
	Absorption band, third from .....	3886—3947	2573—2533
	„ „ fourth from .....	3979—4043	2513—2473
	„ „ fifth from .....	4075—4128	2454—2422
	„ „ sixth from .....	4170—4189	2398—2387
	Faint indication of a band, doubtful from .....	4265—4290	2344—2331
	Lines transmitted 4291 to .....	4555	2195
4	Absorption band, second from .....	3802—3847·5	2630—2599
	„ „ third from .....	3883—3947	2575—2533
	„ „ fourth from .....	3979—4040	2513—2475
	„ „ fifth from .....	4075—4122·5	2454—2426
	„ „ sixth from .....	4170—4215	2398—2372
	Very faint indication of a band, doubtful from .....	4266—4291	2344—2330
	Lines of cadmium transmitted 4291 to .....	4555	2195
3 }	The description applies to both these spectra.		
2 }	Absorption band, second from .....	3812—3847·5	2623—2599
	„ „ third from .....	3915—3937	2554—2540
	„ „ fourth from .....	3995—4030	2503—2480
	„ „ fifth from .....	4100—4120	2439—2427
	„ „ sixth from .....	4190—4210	2386—2375
	Lines of cadmium transmitted with continuous rays to .....	4555	2195
1	Absorption band, second from .....	3819—3847·5	2618—2599
	„ „ third from .....	3915—3934	2554—2541
	„ „ fourth from .....	4004—4024	2497—2485
	„ „ fifth from .....	4103—4116	2437—2429
	„ „ sixth from .....	4202—4208·5	2379—2376
	Continuous spectrum to .....	4555	2195

A remarkable feature of this spectrum not previously so well observed is that the absorption bands are sharpest where the rays are of shorter wave-length, and are gradually weakened in the opposite

direction, as if they were groups of lines closer together and stronger on the side where the rays are of smallest wave-length.

It is perhaps worth while to draw attention to a slight mistake on p. 364 of Herr Pauer's paper; he credits Müller with work on the ultra-violet rays, but the author referred to is undoubtedly the late Dr. William Allen Miller. It has been explained also by Professor W. R. Dunstan, whom he mentions as having investigated ultra-violet absorption spectra, that certain work was in error attributed to him (*Chemical News*, 1891, 63, 309; 1891, 64, 10 and 212).

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## LXXIV.—On *Myrticolorin*, the Yellow Dye Material of *Eucalyptus* Leaves.

By HENRY G. SMITH.

IN the leaves of *Eucalyptus macrorhyncha*, a yellow dye exists in large quantity. From preliminary examination of a small portion of this material, it was evident that the dyeing substance was allied to, if it was not, quercetin. As the discovery was thought to be of some importance to Australia, an announcement was made to the Royal Society of New South Wales (*Proc. Roy. Soc. N.S.W.*, 1897).

It was named myrticolorin as being derived from the Myrtaceæ, to which natural order the Eucalypts belong.

I am indebted to my colleague, Mr. R. T. Baker, the botanist to this Museum, for the description of this tree and its habitat, as too much care cannot be taken in the diagnosis of the several species of this difficult genus, there being in New South Wales alone nearly sixty distinct species of Eucalypts, and many of these differing widely in their chemical constituents. *Eucalyptus macrorhyncha*, F. v. M., is the "red stringy bark" of New South Wales and the ordinary "stringy bark tree" of Victoria. It has a rather extensive range in both colonies, being found in all the principal mountainous country districts.

It is a fair sized tree, rarely exceeding 200 feet in height; the timber is inferior in quality to the "white stringy bark," *E. eugeinoides*, Sieb., and is mostly tinged with red, and is thus easily distinguished from timber of the other stringy barks. It has a very thick, red fibrous bark, and is deeply furrowed. The buds and fruits are very characteristic and cannot well be confused with any other species of *Eucalyptus*; its nearest affinity is perhaps *E. capitellata*, Sm., the "brown stringy bark."

It is figured and described by Baron v. Mueller in his *Eucalyptographia*, Dec. I, and described also in *B. Fl.* : III., 207.

From laboratory experiments, it was found that 10 per cent. of myrticolorin existed in the leaves of this tree under what appears at present to be the most favourable conditions. Commercially, myrticolorin may be extracted with the greatest simplicity.

For the purpose of this research, the crude material was purified by dissolving in boiling water and allowing it to crystallise out, which it readily does as the water cools, forming a semi-solid mass ; this process was repeated two or three times. The myrticolorin was then separated, dried, finely powdered, extracted in a Soxhlet's apparatus with ether until nothing more was dissolved ; the chlorophyll, &c., was thus removed, the ether being of a bright green colour. The powder was then dried and boiled in absolute alcohol, filtering while hot, by which means the colouring substance was separated from the remaining impurities, consisting principally of inorganic salts ; the alcoholic extract thus obtained was evaporated to a small bulk, poured into water, and the remaining alcohol removed by boiling ; on standing, the yellow product crystallised out as usual, and was collected, recrystallised from dilute alcohol, and finally twice from boiling water.

As thus prepared, it was of a pale yellow colour, almost insoluble in cold water, and not very readily soluble in hot water. It dissolved in alkalis with an orange colour ; the aqueous solution gave a yellow coloration with lead acetate, and a dark green coloration with ferric chloride.

Although showing signs of melting at  $179^{\circ}$ , yet it did not melt below  $185^{\circ}$ , at which temperature it formed a thick treacly mass of a dark brown colour.

Myrticolorin reacts with the haloid acids in acetic acid (the method described by A. G. Perkin being used) and also with sulphuric acid, the glucoside being hydrolysed and salts of quercetin containing one molecule of the acid being formed.

The analyses, on material dried at  $130^{\circ}$ , gave the following results, four determinations being given from the large number made.

0.1766 gave 0.3449  $\text{CO}_2$  and 0.0797  $\text{H}_2\text{O}$ . C = 53.26 ; H = 5.02.

0.1932 „ 0.3768  $\text{CO}_2$  „ 0.0874  $\text{H}_2\text{O}$ . C = 53.19 ; H = 5.03.

0.1768 „ 0.3445  $\text{CO}_2$  „ 0.0792  $\text{H}_2\text{O}$ . C = 53.15 ; H = 4.98.

0.2244 „ 0.4378  $\text{CO}_2$  „ 0.0989  $\text{H}_2\text{O}$ . C = 53.21 ; H = 4.89.

$\text{C}_{27}\text{H}_{28}\text{O}_{16}$  requires 53.29 C, and 4.61 H per cent.

Myrticolorin after being dried at the above temperature is very hygroscopic.

As the substance is undoubtedly a glucoside, a portion was taken for decomposition with acid :—1.4353 grams was dissolved in three-

quarters of a litre of water, 7 c.c. of sulphuric acid added, and the whole boiled for 2 hours; when cold, the precipitate was collected, washed with water, dried, and heated to  $160^{\circ}$ ; 0.6998 gram was thus obtained, equal to 48.76 per cent.

0.6068 gram under the same conditions, but with less acid, gave 0.2955 gram, equal to 48.7 per cent.

On analysing the glistening, yellow substance so obtained, it gave the following results.

0.1216 gave 0.2672  $\text{CO}_2$  and 0.0434  $\text{H}_2\text{O}$ . C = 59.93; H = 3.96.

0.1337 „ 0.2924  $\text{CO}_2$  „ 0.0468  $\text{H}_2\text{O}$ . C = 59.64; H = 3.89.

$\text{C}_{15}\text{H}_{10}\text{O}_7$  requires C = 59.6; H = 3.31 per cent.

Although almost insoluble in water, it was fairly soluble in alcohol and the alcoholic solution gave a dark green coloration with ferric chloride, and a brick-red precipitate with lead acetate.

The acetyl derivative, prepared by the usual method, gave a colourless, crystalline product melting at  $190^{\circ}$ .

To investigate the products of decomposition with alkalis, the substance was heated with potash for half-an-hour at  $180$ — $200^{\circ}$ ; the product was dissolved in water, slightly acidified, and extracted with ether; the ether, on evaporation, left a crystalline substance, which, when dissolved in water and tested with hydrochloric acid and fir-wood, gave the phloroglucinol reaction; lead acetate was then added, the precipitate removed, decomposed with sulphuric acid and extracted with ether; the crystalline product thus obtained gave all the reactions of protocathechuic acid, and melted at  $194$ — $196^{\circ}$ . The filtrate from the lead precipitate was acidified with sulphuric acid and extracted with ether; the residue from this gave the phloroglucinol reaction. The products of decomposition were, therefore, *protocatechuic* acid and *phloroglucinol*.

*Hydrolysis by Sulphuric Acid*.—Sulphuric acid was added to a saturated solution of the colouring matter in boiling acetic acid; on cooling, an orange-coloured compound separated, which was collected, pressed as dry as possible, and further dried on a porous plate; it was then suspended in water for 24 hours; the regenerated colouring matter was collected, dried, and weighed, and the sulphuric acid left in solution was determined with barium chloride in the usual way.

The regenerated material weighed 0.085.  $\text{BaSO}_4$  obtained = 0.0677 =  $\text{H}_2\text{SO}_4$  0.0285.

$\text{H}_2\text{SO}_4$  = 25.11, colouring substance 74.89.

$\text{C}_{15}\text{H}_{10}\text{O}_7$ ,  $\text{H}_2\text{SO}_4$  requires  $\text{H}_2\text{SO}_4$ , 24.5; quercetin, 75.5 per cent.

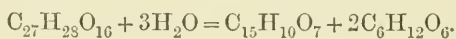
From these results, it appears that the colouring matter obtained by



the decomposition of myrticolorin is quercetin, and that the dye material of eucalyptus leaves is a glucoside of quercetin.

*The Sugar.*—To determine the character of the sugar, the filtrates from the quantitative determinations of the quercetin were neutralised with barium carbonate, filtered, the solution evaporated, and the sugar thus obtained purified. The sugar was a syrup which did not solidify on standing for some weeks; under the microscope, however, square tabular and prismatic crystals were seen; the sugar reduced Fehling's solution and was readily decomposed by yeast. When heated with phenylhydrazine acetate and sodium acetate, an osazone was formed consisting of golden-yellow crystals which softened at  $170^{\circ}$  and melted and slightly decomposed at  $180^{\circ}$  when slowly heated; but when heated rapidly, melted with rapid decomposition at  $190^{\circ}$ . The osazone of galactose melts near this temperature and with the same peculiarities.

From the above determinations it is evident that myrticolorin, when decomposed with acid, gives quercetin and a glucose, and from the analysis the equation may be represented as follows.



This requires 49.67 per cent. of quercetin, whilst but 48.76 per cent. had been obtained by ordinary analysis, as described. It was necessary to account for this discrepancy, because of its importance, as we already know two glucosides of quercetin with regard to which myrticolorin would occupy the intermediate position, namely, *Osyritrin*, obtained from the leaves of the Cape sumach, *Colpoön compressum*, described by Mr. A. G. Perkin (Trans., 71, 1897, 1132), which has the formula  $\text{C}_{27}\text{H}_{30}\text{O}_{17}$ , and *Viola quercitrin*, described by Mandelin (*Jahresber.*, 1883, 1369), obtained from the flowers of *Viola tricolor variensis*, having the formula  $\text{C}_{27}\text{H}_{26}\text{O}_{15}$  (corrected for the present formula of quercetin by Mr. Perkin in the paper above quoted). These three glucosides require the following percentages of carbon.

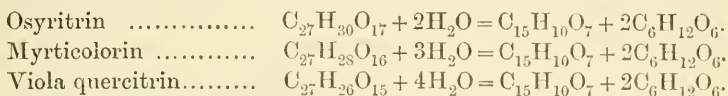
<i>Osyritrin</i> .....	$\text{C}_{27}\text{H}_{30}\text{O}_{17}$ requires	51.76.
<i>Myrticolorin</i> .....	$\text{C}_{27}\text{H}_{25}\text{O}_{16}$ "	53.29.
<i>Viola quercitrin</i> .....	$\text{C}_{27}\text{H}_{26}\text{O}_{15}$ "	54.91.

and they also require the following percentages of quercetin: *Osyritrin* 48.24; *Myrticolorin*, 49.67; *Viola quercitrin*, 51.19.

Fresh analyses on specially prepared myrticolorin always gave numbers approximating to 53 per cent. of carbon. Attention was then directed to the acid filtrate from the quercetin determination, and it was found that, on again boiling and evaporating down, a further precipitate of quercetin could be obtained on standing. A fresh determination was then made by dissolving 0.8842 gram of myrticolorin in 600 c.c. of water, adding 5 c.c. of sulphuric acid, and

keeping the solution just boiling for 3 hours, allowing the water to diminish to 300 c.c. After standing 18 hours, the quercetin was removed washed with water, dried, and heated to 160°. The quercetin obtained amounted to 0.4408 gram = 49.85 per cent. It appears, therefore, that three hours boiling is necessary to decompose the whole of the glucoside.

The foregoing results show that *Myrticolorin* fills the gap between *Osyritrin* and *Viola quercitrin*, and the decomposition with acid of these three substances may be represented by the following formulæ.



*Myrticolorin* is, therefore, a new glucoside of quercetin.

Mr. A. G. Perkin kindly forwarded to me a portion of *Osyritrin*, and the resemblance between that substance and *Myrticolorin* is very marked; in colour, melting point, reactions with reagents, and dyeing power, no differences could be detected, the colours given on striped calico by the two substances being identical under the same conditions.

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## LXXV.—*Chemical Properties of Concentrated Solutions of certain Salts. Part II. Double Potassium Succinates.*

By WILLIAM COLEBROOK REYNOLDS, A.R.C.S.

IN a previous communication (Trans., 1898, 73, 262), I have shown that when the soluble salts of several of the metals are added to a very concentrated solution of potassium carbonate, crystalline double carbonates of the metal and potassium, more or less soluble in the solution, are obtained, instead of the insoluble carbonates or basic carbonates, and that these compounds are decomposed by water to an extent depending on the quantity of water added. For comparison with the above, I have studied the behaviour of the same salts with a concentrated solution of potassium succinate (sp. gr. = 1.42), this salt being chosen because it is very soluble, whilst the normal succinates of the metals, except those of the alkalis and magnesium, are almost insoluble in water.

The addition of soluble salts to this liquid results in several cases in the formation of a solution from which, if a sufficient amount of the soluble salt has been added, crystalline double succinates, as a

rule, separate. As in the case of the carbonates, the addition of water to the solutions of the double salts causes decomposition and separation of hydrated metallic succinates. This rapid decomposition by water makes the isolation of pure specimens of the salts difficult, and, as before, after draining on a Buchner filter plate with the aid of a water pump, the mother liquor was mechanically displaced by a mixture of glycerol and alcohol, and the crystals were finally washed with alcohol.

*Copper potassium succinate* can be easily obtained in small, blue prisms by dissolving copper acetate in the hot solution of potassium carbonate and allowing the mixture to stand a short time.

	$\text{CuC}_4\text{H}_4\text{O}_4$	$\text{K}_2\text{C}_4\text{H}_4\text{O}_4$	$\text{H}_2\text{O}$
Found .....	29.86	64.2	6.04
Calculated for $\text{CuK}_4(\text{C}_4\text{H}_4\text{O}_4)_3 + 2\text{H}_2\text{O}$	29.68	64.36	5.96

*Nickel potassium succinate* can be prepared by adding the finely powdered nitrate or chloride to the hot solution of potassium carbonate (1 gram to each 20 c.c.), the salt separating after a few minutes from the still warm liquid.

	$\text{NiC}_4\text{H}_4\text{O}_4$	$\text{K}_2\text{C}_4\text{H}_4\text{O}_4$	$\text{H}_2\text{O}$
Found .....	30.30	67.00	2.77
Calculated for $\text{NiK}_4(\text{C}_4\text{H}_4\text{O}_4)_3 + \text{H}_2\text{O}$	30.08	66.85	3.07

*Cobalt potassium succinate* can be prepared from the nitrate as above (1 gram to each 16 c.c.).

	$\text{CoC}_4\text{H}_4\text{O}_4$	$\text{K}_2\text{C}_4\text{H}_4\text{O}_4$	$\text{H}_2\text{O}$
Found .....	47.52	51.97	0.37
Calculated for $\text{CoK}_2(\text{C}_4\text{H}_4\text{O}_4)_2$	47.34	52.66	nil

*Zinc potassium succinate* can be prepared by adding the powdered acetate to the solution and allowing the mixture to remain until it crystallises.

	$\text{ZnC}_4\text{H}_4\text{O}_4$	$\text{K}_2\text{C}_4\text{H}_4\text{O}_4$	$\text{H}_2\text{O}$
Found .....	47.12	50.59	2.34
Calculated for $(\text{ZnK}_2\text{C}_4\text{H}_4\text{O}_4)_2 + \text{H}_2\text{O}$	46.96	50.90	2.14

*Lead potassium succinate* can be prepared by adding powdered lead acetate slowly, with stirring, to the hot solution; the crystals separate in a minute or two.

	$\text{PbC}_4\text{H}_4\text{O}_4$	$\text{K}_2\text{C}_4\text{H}_4\text{O}_4$	$\text{H}_2\text{O}$
Found .....	73.45	22.35	4.25
Calculated for $\text{Pb}_2\text{K}_2(\text{C}_4\text{H}_4\text{O}_4)_3 + 2\text{H}_2\text{O}$	73.73	22.16	4.11

*Calcium potassium succinate* can be prepared from calcium acetate in the same way as the lead compound.

	$\text{CaC}_4\text{H}_4\text{O}_4$	$\text{K}_2\text{C}_4\text{H}_4\text{O}_4$	$\text{H}_2\text{O}$
Found .....	57.60	35.37	6.87
Calculated for $\text{Ca}_2\text{K}_2(\text{C}_4\text{H}_4\text{O}_4)_3 + 2\text{H}_2\text{O}$	57.55	35.82	6.63

On adding manganese acetate\* to the solution, the double compound which is formed is so soluble that, although a strong solution was prepared and allowed to stand during some weeks, no crystals separated. From a somewhat diluted solution, an amorphous, hydrated double succinate of manganese and potassium separated slowly, but the composition of the precipitate was not constant.

Ferrous chloride will dissolve in some quantity in the solution, but the crystals which separate after some time are those of a hydrated ferrous succinate, and do not contain potassium; a similar compound of cobalt can be obtained from a slightly diluted hot solution.

Soluble salts of barium, bismuth, silver, and mercury do not dissolve in the solution and the simple hydrated succinates are formed.

Magnesium succinate is scarcely comparable with the above, since it is soluble in water, but on adding a considerable quantity to the saturated solution of potassium succinate and setting aside for some days, a double succinate,  $\text{MgK}_2(\text{C}_4\text{H}_4\text{O}_4)_2 + 5\text{H}_2\text{O}$ , is deposited as previously noted by Doepping (*Annalen*, 1843, 47, 273).

Two of the above double succinates, those of nickel and copper, are of some interest when the question of the constitution of such compounds is considered. The double succinate, carbonate, sulphate, and oxalate of cobalt and potassium, for instance, may be regarded either as constituted as follows



where  $\text{A}'' = \text{C}_4\text{H}_4\text{O}_4$ ,  $\text{CO}_3$ ,  $\text{SO}_4$ , or  $\text{C}_2\text{O}_4$ , or it may be supposed that they consist of molecular compounds of the two salts, in which they are possibly linked through the oxygen atoms, an assumption that has been made to account for cases such as the molecular association in many liquids containing oxygen, water of crystallisation, the double acetates, and double nitrates. The nickel and copper compounds show that the latter view is the more probable, for their composition,  $\text{K}_4\text{R}(\text{C}_4\text{H}_4\text{O}_4)_3$ , is such that they cannot be represented by a structural formula analogous to that written above for the cobalt salt.

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LXXVI.—*Researches on the Terpenes. III. Halogen Derivatives of Fenchone and their Reactions.*

By JOHN ADDYMAN GARDNER, M.A., and GEORGE BERTRAM COCKBURN, B.A.

IN a former paper (Trans., 1897, 71, 1156) we described a compound of the formula  $C_{10}H_{14}ClPO(OH)_2$ , which we named chlorofenchenephosphonic acid, produced by acting on fenchone with phosphorus pentachloride in the cold, and subsequently treating the product with water. In this communication we give a further account of the properties of this substance, and also describe the halogen derivatives of fenchene produced at the same time.

*α and β-Chlorofenchene Hydrochlorides.*—Fifty grams of fenchone were mixed with 200 grams of phosphorus pentachloride in a flask closed with a calcium chloride tube, and allowed to stand at a temperature of 35–40°. A very slow action took place with gradual evolution of hydrogen chloride, and after standing for six weeks the contents of the flask were poured on to ice and left to stand until all the phosphorus chlorides were decomposed. The oil obtained in this way was shaken with a solution of sodium carbonate to extract the chlorofenchenephosphonic acid, and distilled in a current of steam. The oil which passed over was separated from the water, dried, and subjected to careful fractional distillation under a pressure of 16 mm. Two main fractions were obtained, one boiling at 105–110°, and the other at 85–90°; the latter, which solidified in the condenser, was chlorofenchene, and is described later (p. 705).

The fraction of higher boiling point was a colourless oil, which, after refractionation, boiled at 107–109° under 16 mm., but decomposed on distillation under the ordinary atmospheric pressure. An estimation of the chlorine gave the following result.

0.2639 gave 0.3615 AgCl. Cl = 33.89.

$C_{10}H_{16}Cl_2$  requires 34.23 per cent.

In other experiments, the oil left after extraction with sodium carbonate solution, instead of being distilled with steam, was taken up in ether, dried, and, after evaporating off the ether, distilled under diminished pressure.

No chlorofenchene was obtained, and the bulk of the liquid passed over at 105–110°, and had practically the same percentage of chlorine. It was then heated to 100° with aniline for a few minutes; on cooling, some aniline hydrochloride crystallised out, and the liquid was then acidified with hydrochloric acid and distilled in steam, when a



small amount of chlorofenchene was obtained, together with an oil which again distilled at 105—110° under 16 mm. pressure. This was again boiled with aniline, but very little action took place, and, on repeating the treatment just described, no more chlorofenchene was obtained, and the oil passed over apparently unchanged. A very small amount of a crystalline substance, not volatile in steam, was, however, found to be mixed with the aniline hydrochloride; it was separated by taking advantage of its insolubility in water and its slight solubility in alcohol. It crystallised from alcohol in yellowish needles, which melted at 120°, but the quantity was too small for complete purification. The following analyses of the partially purified substance show that it very probably possesses the constitution  $C_{10}H_{16}Cl \cdot NHC_6H_5$ . The presence of nitrogen was proved qualitatively.

0.1798 gave 0.484  $CO_2$  and 0.1341  $H_2O$ .  $C = 73.41$ ;  $H = 8.28$ .

0.2059 „ 0.1029  $AgCl$ .  $Cl = 12.3$ .

$C_{10}H_{16}Cl \cdot NH \cdot C_6H_5$  requires  $C = 72.89$ ;  $H = 8.35$ ;  $Cl = 13.43$  per cent.

The oil boiling at 105—110°, which had proved to be stable as regards aniline, was then heated with zinc dust and glacial acetic acid, by which means hydrogen chloride was removed, but this was effected only with difficulty.

Twenty-five grams of the oil were heated with 18 grams of zinc dust and an excess of glacial acetic acid over a free flame. After boiling during 36 hours, the product was distilled with steam, and the oil which passed over fractionated under reduced pressure. A considerable portion of the oil remained unchanged, as was shown by the boiling point and by a chlorine estimation, but some was converted into chlorofenchene. On again treating the unchanged oil in the same way, a further portion of chlorofenchene was obtained. It seems clear then, from these experiments, that the first action of the pentachloride is to replace the oxygen of the fenchone by chlorine, and that the substance,  $C_{10}H_{16}Cl_2$ , so produced, consists of a mixture of two isomerides, which we propose to name  $\alpha$ - and  $\beta$ -chlorofenchene hydrochlorides. The two substances are too nearly equal in boiling point to admit of their being separated by distillation, but they differ considerably in stability, the one losing hydrogen chloride even by distillation in steam, and readily by the action of aniline, whilst the other is stable towards aniline, and only loses hydrogen chloride very slowly and with difficulty when treated with zinc dust and glacial acetic acid. Both isomerides yield apparently the same chlorofenchene.

*Chlorofenchene*.—Chlorofenchene is a solid, crystalline substance, which cannot be purified by crystallisation owing to its great solubility, but can be readily purified by distillation under diminished pressure. It boils at 80—83° under a pressure of 16 mm., and at

190—192° at the ordinary pressure, but in the latter case it seems to undergo some slight decomposition, as the melting point is lowered and it becomes more liquid. It is extremely soluble in alcohol, ether, benzene, light petroleum, chloroform, and carbon bisulphide; exposure to the vapour of the latter being sufficient to cause its liquefaction.

On analysis, it gave the following results.

0.1916 gave 0.4946  $\text{CO}_2$  and 0.1549  $\text{H}_2\text{O}$ .  $\text{C} = 70.4$ ;  $\text{H} = 8.98$ .

0.2205 „ 0.1831  $\text{AgCl}$ .  $\text{Cl} = 20.52$ .

$\text{C}_{10}\text{H}_{15}\text{Cl}$  requires  $\text{C} = 70.42$ ;  $\text{H} = 8.80$ ;  $\text{Cl} = 20.77$ .

The yield obtained from the  $\alpha$ , or easily decomposable, chlorofenylene hydrochloride was very small, probably owing to its having been converted into chlorofenylene phosphonic acid. It could not, therefore, be obtained in quite the same state of purity as that prepared from the  $\beta$ -hydrochloride by the action of zinc dust and glacial acetic acid. The two specimens, however, differ so slightly in their properties that there can be no doubt as to their identity.

From  $\alpha$ -hydrochloride.

M. p. 76—78°.

B. p. 189—191.

$[\alpha]_D + 38.57^\circ$ .

Pure subs. from  $\beta$ -hydrochloride.

M. p. 89—90°.

B. p. 190—192.

$[\alpha]_D + 35.92^\circ$ .

Monochlorofenylene behaves as a saturated compound, being unacted on by potassium permanganate solution in the cold, and attacked by bromine with evolution of hydrogen bromide. It is very similar in appearance to the chlorocamphene obtained from camphor by an analogous method, but differs from it considerably in boiling point, specific rotatory power, and chemical properties.

Chlorocamphene.

B. p. 202°.

$[\alpha]_D - 29.3^\circ$ .

Chlorofenylene.

190—192°.

$[\alpha]_D + 35.92^\circ$ .

*Action of Sulphuric Acid.*—We had not a sufficient quantity of chlorofenylene for a satisfactory comparison of the action of sulphuric acid on it with that on chlorocamphene, which yields camphenol (Marsh and Gardner, Trans., 1897, 71, 290). As, however, camphenol may be obtained both from chlorocamphene and from  $\alpha$ - and  $\beta$ -chlorocamphene hydrochlorides, we thought that it would be equally satisfactory to try the action of sulphuric acid on the  $\beta$ -chlorofenylene hydrochloride. Thirty grams of this substance were therefore added to 300 grams of sulphuric acid previously diluted with 5 per cent. of water, and the mixture gently warmed on the top of the water oven; the action was brisk and much hydrogen chloride, as well as some sulphur dioxide, was given off, with frothing. The black liquid was poured into an excess of water, and distilled in steam, when about 3

grams of oil passed over, and a tarry mass was left in the distilling flask. The oil was extracted with ether, dried and distilled, when it came over within a range of  $60^{\circ}$ , boiling from  $180$ — $240^{\circ}$ . The liquid so obtained was attacked by bromine with evolution of hydrogen bromide, but did not react with phosphorus pentachloride; probably, therefore, it contained neither camphenol nor any substance analogous to it. The liquid contained some chlorine, which was removable by metallic sodium.

As we were unable to compare the action of sulphuric acid on chlorofenchene itself with that on chlorocamphene, we tried the action of phosphorus pentachloride on a small quantity of each. Three to four grams of chlorofenchene were intimately mixed with a large excess of the pentachloride by rubbing together in a mortar; the chlorofenchene liquefied on contact with the phosphorus pentachloride, and the product obtained did not set or harden on standing. After remaining in a dry atmosphere for three days, it was poured into water and allowed to stand until all the phosphorus chloride compounds had been decomposed. The oil left at the bottom of the dish was then mixed with a dilute solution of caustic soda, and distilled in steam, when an oil passed over equal in weight to more than half the chlorofenchene taken. The clear solution left in the distilling flask was acidified with hydrochloric acid and extracted with ether; the ethereal solution was evaporated to dryness, and the yellow-coloured, solid residue dissolved in boiling water, in which it was only difficultly soluble. On evaporating and cooling, crystals separated similar in appearance to chlorofenchene phosphonic acid; these were recrystallised from water, and then melted at  $196^{\circ}$ . They consisted of chlorofenchene phosphonic acid, and were decomposed by bromine water, giving an oil volatile in steam and phosphoric acid in solution. The action of phosphorus pentachloride on chlorofenchene takes place then very slowly and gives the compound  $C_{10}H_{14}ClPCl_4$ , which on decomposition with water yields the acid  $C_{10}H_{14}ClPO(OH)_2$ .

Chlorocamphene under similar circumstances behaved quite differently to chlorofenchene. It did not liquefy on mixing with the pentachloride, but remained quite solid. After standing for three days, the mixture was treated exactly as described above. The action was apparently slow, for half the chlorofenchene was recovered on distilling with steam. The liquid which remained in the distilling flask, after being filtered, was acidified and extracted with ether. No chlorofenchene phosphonic acid was obtained, but two acids which we have not yet investigated.

*Action of Bromine on Chlorofenchene phosphonic Acid.*—Bromine water was added to an aqueous solution of sodium chlorofenchene phosphonate until it was no longer decolorised, the turbid liquid

obtained treated with a small quantity of sodium carbonate solution to remove the excess of free bromine, and then extracted with chloroform. After the chloroform had been evaporated off, the extract was distilled under diminished pressure, when the whole of the product passed over at  $113-114^{\circ}$  under 11 mm. pressure. It was a colourless oil which decomposed on distillation at the ordinary pressure, giving off bromine.

The liquid had a specific gravity  $1.38039$  at  $16^{\circ}$ , and specific rotatory power  $[\alpha]_D = -8.42^{\circ}$ .

On analysis, the following results were obtained.

$0.2879$  gave  $0.5034$   $\text{CO}_2$  and  $0.1471$   $\text{H}_2\text{O}$ .  $\text{C} = 47.68$  ;  $\text{H} = 5.67$ .

$0.3613$  ,,  $0.481$   $\text{AgCl} + \text{AgBr}$ .

$0.4810$   $\text{AgCl} + \text{AgBr}$  gave  $0.3138$   $\text{Ag}$ .  $\text{Br} = 32.1$  ;  $\text{Cl} = 14.3$ .

$\text{C}_{10}\text{H}_{14}\text{ClBr}$  requires  $\text{C} = 48.09$  ;  $\text{H} = 5.61$  ;  $\text{Br} = 32.00$  ;  $\text{Cl} = 14.27$ .

A determination of the quantity of sodium phosphate liberated by the action of bromine was made, and the result showed that the action was practically quantitative. This substance, which we may call chlorobromofenchene, although decomposed on heating, is very stable towards reagents, the chlorine and bromine atoms being very firmly bound in the molecule.

Neither zinc dust and acetic acid, nor aniline, nor sodium in methyl alcohol solution, are capable of removing either of the halogen atoms, and the product obtained after treatment with these various reagents possessed the same boiling point, and had the same percentage of halogens as before.

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## LXXVII.—*Researches on the Terpenes. IV. On the Oxidation of Fenchone.*

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FENCHONE appears to be very much more stable towards oxidising agents than its isomeride camphor, but when action takes place much more complete breaking down of the molecule is effected. Using nitric acid, we have succeeded in isolating from the product, in addition to unchanged fenchone, the following substances: isocamphoronic, dimethyltricarballic, dimethylmalonic, isobutyric and acetic acids, and nitrofenchone.

Fenchone (50 grams) was mixed with concentrated nitric acid (200

c.c.) and heated in long-necked flasks on the water bath for 6 days, more acid (100 c.c. altogether) being added from time to time as the action became too slow. The acid liquid thus obtained was distilled with steam, and the layer of unattacked fenchone in the receiver, amounting to 50 per cent. of the ketone originally taken, was separated from the aqueous portion, which was then neutralised with sodium carbonate. This solution was evaporated to a small bulk, acidified with oxalic acid, again distilled with steam, and the distillate neutralised with baryta and evaporated to dryness. 70.9 grams of barium salts were obtained from 300 grams of fenchone actually oxidised. This mixture of barium salts was fractionally acidified with sulphuric acid, the product being distilled in steam after each addition of acid; the distillates thus obtained were neutralised with sodium carbonate, and again subjected to a similar treatment. The various fractions were now neutralised, precipitated with silver nitrate, and the silver salts so obtained purified by recrystallisation from hot water. On analysis, the first and last fractions gave the following numbers.

First fraction: 0.2461 gave 0.1356 Ag.  $\text{Ag} = 55.1$ .

$\text{C}_4\text{H}_7\text{AgO}_2$  requires  $\text{Ag} = 55.3$  per cent.

Last fraction: 0.2305 gave 0.1481 Ag.  $\text{Ag} = 64.2$ .

$\text{C}_2\text{H}_3\text{AgO}_2$  requires  $\text{Ag} = 64.59$  per cent.

The free acid from the first fractions was characterised as isobutyric acid by its solubility in water.

The portion of the oxidation product not volatile with steam was evaporated to a small bulk on the water bath, and then dissolved in a moderate amount of concentrated nitric acid. On standing for a few days, a considerable quantity of crystalline matter separated, which was filtered off. A further crop of crystals was obtained from the filtrate on longer standing. This solid matter was washed with chloroform to remove adhering oil, and repeatedly fractionally crystallised from strong nitric acid. By this means two substances were obtained, one melting between  $145^\circ$  and  $155^\circ$ , and the other between  $185^\circ$  and  $190^\circ$ . The substance of higher melting point was now crystallised from water, from which it readily separated, and after several crystallisations melted sharply at  $190^\circ$ . It was dimethylmalonic acid, and on analysis gave the following numbers.

0.2159 gave 0.3595  $\text{CO}_2$  and 0.1209  $\text{H}_2\text{O}$ .  $\text{C} = 45.41$ ;  $\text{H} = 6.22$ .

$\text{C}_5\text{H}_8\text{O}_4$  requires  $\text{C} = 45.45$ ;  $\text{H} = 6.06$  per cent.

On titrating the acid with ammonia (1 c.c. = 0.00334  $\text{NH}_3$ ), 0.4859 required 37.52 c.c.

Mol. wt. found = 131.96.  $\text{C}_5\text{H}_8\text{O}_4$  requires 132.

On heating strongly, the acid decomposed, giving isobutyric acid.



The substance melting at 145—155° was extremely soluble in water, ether, alcohol, and acetone, and often separated as an oil from these solvents. It was purified by repeatedly crystallising from strong nitric acid, and finally by precipitating the ethereal solution with chloroform. The pure substance melted at 152°, and proved to be dimethyltricarballic acid.

On analysis, it gave the following numbers.

0.2156 gave 0.3708 CO<sub>2</sub> and 0.1163 H<sub>2</sub>O. C = 46.9; H = 5.9.

0.2149 „ 0.3679 CO<sub>2</sub> „ 0.1128 H<sub>2</sub>O. C = 46.69; H = 5.83.

C<sub>8</sub>H<sub>12</sub>O<sub>6</sub> requires C = 47.06; H = 5.88 per cent.

On treatment with acetyl chloride, this acid gave an anhydride, which, after crystallisation from alcohol, melted at 139—141°. On combustion, it gave the following figures.

0.206 gave 0.3883 CO<sub>2</sub> and 0.1097 H<sub>2</sub>O. C = 51.4; H = 5.8.

C<sub>8</sub>H<sub>10</sub>O<sub>5</sub> requires C = 51.61; H = 5.38.

The triethylic salt, prepared from the oily mother liquors from the crystalline acids by a method described later, was a colourless liquid boiling at 172—174° under a pressure of 19 mm. On combustion, it gave the following results.

0.2384 gave 0.5096 CO<sub>2</sub> and 0.1802 H<sub>2</sub>O. C = 58.29; H = 8.4.

C<sub>14</sub>H<sub>24</sub>O<sub>6</sub> requires C = 58.33; H = 8.33 per cent.

The lead salt was prepared as an insoluble powder by precipitating a solution of the sodium salt with lead nitrate; a sample prepared from the acid regenerated from the ethylic salt was analysed.

1.2687 gave 1.1270 PbSO<sub>4</sub>. Pb = 60.58.

2(C<sub>8</sub>H<sub>9</sub>O<sub>6</sub>)Pb<sub>3</sub> requires Pb = 60.59 per cent.

The copper salt was also insoluble, and was obtained as a bulky, gelatinous, bluish-green precipitate, which, when dried, became a dark green, crystalline powder.

The non-crystalline portion of the oxidation product, left after the removal of the above-mentioned acid, was dissolved in water and neutralised with caustic soda, when a small portion remained undissolved. The aqueous solution was precipitated by means of an excess of lead nitrate, and the voluminous precipitate obtained was well washed with hot water and filtered. The precipitate and filtrate were separately acidified with hydrochloric acid, evaporated to dryness on the water bath, and extracted with ether in a Soxhlet's apparatus. After evaporating the ether from these extracts, acid oils were obtained, which could neither be crystallised nor distilled, and were, therefore, converted into the ethylic salts by dissolving them in absolute alcohol, and passing in gaseous hydrogen chloride. The alcoholic

solutions of the ethereal salts thus obtained were poured on a mixture of solid carbonate of soda and ice, when the salts separated as heavy oils, and were extracted with ether and distilled under diminished pressure.

In the case of the ethereal salts derived from the insoluble lead salt, fractions were obtained boiling at  $80-110^{\circ}$ ,  $150-170^{\circ}$ , and  $170-182^{\circ}$ , under 19 mm. pressure. The lower fraction was now fractionated under ordinary pressure, when the bulk of it came over at  $193-196^{\circ}$ . This was ethylic dimethylmalonate, for, on saponification, it gave dimethylmalonic acid, m. p.  $188^{\circ}$ .

On again refractionating the two higher fractions under a pressure of 19 mm., the major portion distilled at  $170-172^{\circ}$ . A combustion showed that this was the ethylic salt of dimethyltricarballic acid. On saponification, it gave the acid melting at  $151-153^{\circ}$ .

The sodium carbonate solution left after the separation of the crude ethereal salts was acidified with hydrochloric acid, evaporated to dryness, and extracted with ether in a Soxhlet's apparatus; on evaporating the ethereal extract, a semi-solid mass was obtained, which was recrystallised from a mixture of chloroform and ether. The white, crystalline substance thus obtained consisted of a mixture of two acids; one of them, which proved to be dimethyltricarballic acid, was exceedingly soluble in ether, whilst the other was much less soluble. The two acids were therefore separated by means of ether, and the less soluble one after recrystallisation from acetic ether melted at  $163-164^{\circ}$ . When pure, it crystallised from either ether or acetic ether in well-defined, colourless, tabular plates, but was insoluble in benzene and chloroform.

On combustion, it gave the following numbers.

- I. 0.2197 gave 0.3967  $\text{CO}_2$  and 0.1290  $\text{H}_2\text{O}$ . C = 49.24; H = 6.52.  
 II. 0.2209 „ 0.4008  $\text{CO}_2$  „ 0.1306  $\text{H}_2\text{O}$ . C = 49.48; H = 6.57  
 $\text{C}_9\text{H}_{14}\text{O}_6$  requires C = 49.54; H = 6.42 per cent.

The silver salt, obtained by precipitating the sodium salt with silver nitrate, was insoluble in cold water, but soluble in hot. On ignition, it gave the following results.

- 0.1719 gave 0.1025 Ag. Ag = 59.62.  
 $\text{C}_9\text{H}_{11}\text{O}_6\text{Ag}_3$  requires Ag = 60.03 per cent.

On heating to boiling with acetyl chloride for some time, the acid remained undissolved and unchanged; on heating, however, at  $100^{\circ}$  in a sealed tube it dissolved, and apparently some hydrogen chloride was formed, but after evaporating the liquid to get rid of acetyl chloride and recrystallising the residue from acetic ether, the melting point was found to be  $160-162^{\circ}$ , so that apparently little action had taken

place. This acid is without doubt Tiemann's isocamphoronic acid, which was previously named hydroxycamphoronic acid by Kachler (*Annalen*, 1878, 191, 143).

The ethylic salts prepared from the oils which gave a soluble lead salt, were small in quantity, and on distillation boiled through a wide range of temperature. On saponification, they yielded only a small amount of solid matter, which we were unable to purify in quantity sufficient for combustion.

The yields of these acids from the amount of fenchone actually attacked in the oxidation process were—dimethyltricarballic acid, 30 per cent.; dimethylmalonic acid, 4 per cent., and isocamphoronic acid, about  $1-1\frac{1}{2}$  per cent.

The oil which remained undissolved after neutralising the non crystalline portion of the oxidation product with caustic soda was extracted with ether, dried, and, after evaporating off the ether, distilled under a pressure of 14 mm., when it passed over between  $135^{\circ}$  and  $160^{\circ}$ . On further fractionation, the bulk came over at  $140-150^{\circ}$ ; this was again separated into further fractions and the largest,  $146-151^{\circ}$ , was analysed.

I. 0.2075 gave 0.4651  $\text{CO}_2$  and 0.1430  $\text{H}_2\text{O}$ .  $\text{C} = 61.15$ ;  $\text{H} = 7.65$ .

II. 0.2769 „ 16.2 c.c. nitrogen at  $19^{\circ}$  and 767 mm.  $\text{N} = 6.8$ .

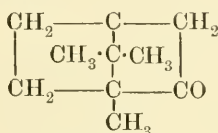
$\text{C}_{10}\text{H}_{15}\text{O} \cdot \text{NO}_2$  requires  $\text{C} = 60.91$ ;  $\text{H} = 7.61$ ;  $\text{N} = 7.1$ .

It was a nitrofenchone, and on reduction with stannous chloride gave a base the hydrochloride of which was very soluble in water and alcohol, but insoluble in ether. It formed a yellow double salt with platinum chloride soluble in water, but difficultly so in alcohol. The quantities were too small for further investigation.

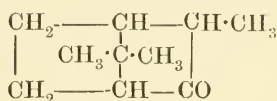
*Theoretical.*—The close analogy, which has been proved by Wallach to exist between camphoroxime and fenchonoxime, campholenic acid, and fencholenic acid, borneol and fenchyl alcohol, bornylamine and fenchylamine, &c., indicate that the formula for fenchone must be very similar to that of camphor. This is also borne out by the experiments on the halogen derivatives of fenchene (*Trans.*, 1898, 73, 704). That this relationship cannot be expressed by a mere difference in the position of the oxygen atom, as in Bredt's original formulæ, was shown by Wallach's conversion of camphor into paracymene and of fenchone into metacymene. The results we have obtained by the oxidation of fenchene (the production of camphopyric acid directly from fenchene without the intermediate formation of camphoic acid, as in the case of camphene), and the acids from fenchone described in this paper, seem to throw some light on this relationship. They do not enable us to definitely decide on a formula for fenchone, but, given the correct formula for camphor, we think they would be sufficient to decide that

of fenchone. Wallach (*Annalen*, 1895, 284, 341) suggested for fenchone the formula  $\begin{array}{c} \text{CH}_3 \cdot \text{CH} - \text{CH} \cdot \text{CH}_2 \\ | \quad | \\ \text{CH}_2 \cdot \text{CH} - \text{CO} \end{array} > \text{C}(\text{CH}_3)_2$ , based mainly on the production of dimethylmalonic acid by oxidation; this formula would not, however, account for the formation of isocamphoronic and dimethyltricarballic acids. The formula proposed by Tiemann (*Ber.*, 1895, 28, 1079—1093) for camphor and fenchone would not, on the other hand, account for the production of camphopyric acid from both fenchene and camphene.

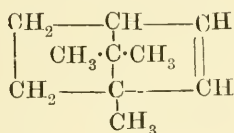
If we assume the truth of Bredt's formulæ for camphor and camphene, the following formulæ would express their relationship to fenchone, &c.



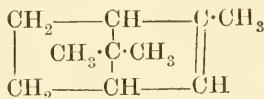
Camphor (Bredt).



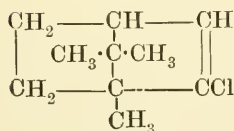
Fenchone.



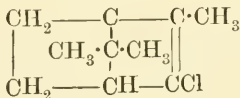
Camphene



Fenchene.



Chlorocamphene.



Chlorofenchene.

These formulæ would account for the production of isocamphoronic, dimethyltricarballic, and dimethylmalonic acids from fenchone, and of camphopyric acid from fenchene without the intermediate formation of camphoic acid. Although these fenchone formulæ express the relationship of fenchone to camphor sufficiently well, they are open to the same objections which have been urged against Bredt's camphor formula. They do not account for the apparent behaviour of camphene, chlorocamphene, and chlorofenchene as saturated compounds, or the isomerism of the  $\alpha$ - and  $\beta$ -chlorocamphene and chlorofenchene hydrochlorides, or explain why camphoic acid is never obtained by the oxidation of camphoric acid.

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LXXVIII.—*Röntgen Ray Photography Applied to Alloys.\**

By CHARLES THOMAS HEYCOCK and FRANCIS HENRY NEVILLE.

WHEN a salt solution is cooled until solid matter begins to form, the process of solidification may, if we exclude the contingency of the formation of definite crystalline hydrates, take place in one of three ways. Let us suppose that we are dealing with a solution of potassium permanganate, where the strong colouring matter of the salt makes the observation of the phenomena easy. Then, if the solidification follows a normal course, and for the sake of simplicity we shall suppose that it does so, we may observe the following cases.

*a.*—If a sufficiently dilute solution be slowly cooled, then at some temperature below zero colourless crystals of ice will begin to form, the whole of the permanganate remaining in solution in the mother liquor. As this residual liquid becomes more concentrated, the ice will form at a continually lower and lower temperature, but when, by the removal of the solvent as ice, a certain concentration of the permanganate has been reached, the permanganate, or conceivably a definite hydrate of it, will begin to solidify together with the water, and no further fall in temperature will be observed until everything has become solid. Thus the process of solidification consists of two stages.

*b.*—The second case occurs when a hot concentrated solution of permanganate is cooled. In this case, the first crystals that form will be pure permanganate, or conceivably a definite hydrate, and only after a considerable quantity of this has solidified at lower and lower temperatures, will ice begin to form, from this point onwards the solidification again taking place at a constant temperature until the whole is solid. The constant temperature during the second stage of *a* is the same as that of the second stage of *b*, the concentration being also the same in both cases.

*c.*—From the above, it is obvious that a solution of permanganate can be prepared of such a strength that its solidification will take place from beginning to end at the constant temperature which marks the second stages of *a* or *b*, the ice and the solid salt forming simultaneously. We may say that such a solution is saturated both with ice and with permanganate when at its freezing point, since, if we attempt to cool it further, both of these substances separate in the same proportion as that in which they are present in the liquid; solu-

\* A brief preliminary notice of this paper was published in the Proceedings of the Chemical Society, 1897, p. 105.



tions of the latter class were first investigated by Guthrie and termed by him "eutectic solutions." Guthrie at one time believed that such solutions and the solid matter formed from them were definite chemical compounds, but this view has since proved to be erroneous.

These three types of solidification can also be studied by the aid of a freezing point curve. When such a curve is traced by experiment for mixtures in every proportion of two substances, the freezing point, or halt in the cooling which marks the separation of solid matter, being taken as the ordinate, and the percentage composition being taken as the abscissa, we find the following to be the simplest case. A branch starts from the melting point of each of the pure substances, the two branches meeting in an angle at their lowest point; there is also a horizontal straight line passing through the intersection of the two branches. The points on one branch correspond to the first stage of *a*, those on the other to the first stage of *b*, whilst the angle corresponds to the case *c*, and the horizontal straight line through it corresponds to the second stages of *a* and *b*.

Several observers have studied the solidification of alloys by plotting the freezing point curves, but, on account of the opacity of all alloys and of other difficulties, it has hitherto been impossible to follow and to study the formation of crystals as in the above-mentioned case of permanganate. The remarkable differences, however, in transparency to the Röntgen rays shown by different metals led us to hope that after slowly cooling a liquid alloy of two metals, one of high and the other of low atomic weight, we might be able to photograph *through* the solid alloy and examine the crystalline separations that had taken place. This method has proved so far of somewhat limited applicability, but in several cases we have been successful. The present paper contains results obtained with the following pairs of metals; gold and sodium, gold and aluminium, copper and aluminium, silver and aluminium. The structure of solid alloys has usually been studied with the aid of the microscope on account of the minute character of the separations which occur, but as skiagraphs admit of but little subsequent magnification, it was indispensable for our purpose that the detail, that is to say the individual crystals in the alloy, should be large. We obtained this result by making the process of solidification a very gradual one; an account of the cooling apparatus will be found at the end of the paper. The alloys were usually allowed to cool and solidify in cylindrical crucibles, the solid cylinders thus obtained being nearly an inch in diameter and from 2 to 4 inches long. Vertical and horizontal sections of these cylinders were cut, and when possible turned down to a thickness of less than a millimetre and polished. These sections were laid on an Ilford plate enclosed in a light-tight

envelope, and exposed to the Röntgen rays for periods varying from five minutes to an hour.

The figures in the plate accompanying this paper (p. 722) correspond to positives, and therefore the lighter details indicate the most transparent metal. The figures are the natural size of the objects; they should be examined by means of a pocket lens.

### *Gold-Sodium Alloys.*

In the Journal of the Chemical Society for 1889 (p. 668), we traced the changes in the freezing point of sodium caused by the addition of gold; we found that the eutectic alloy contained about 23 per cent. of gold and had a freezing point of  $82^{\circ}$  C. Since these metals differ so much in their transparency to the Röntgen rays, it seemed well to commence with them.

To make the alloys, weighed quantities of sodium were melted and weighed quantities of gold added. The alloy was then heated, either under a mineral oil or in a sealed vacuum tube, with constant agitation, to a temperature sufficient to dissolve all the gold. Clean portions of the alloy were then sucked up with a pipette and transferred to a wide test-tube immersed vertically in a boiling brine bath, sufficient precautions being taken to avoid any danger of oxidation of the sodium, either by contact with the air or with moisture. The bath was kept constantly stirred by a current of air, and allowed to cool very slowly during a period of 24 hours or more. From the solid cylinder of alloy thus obtained, horizontal and vertical sections were cut, these sections being usually from 1 to 2 millimetres in thickness. Each section was immediately placed between sheets of very thin aluminium foil and the edges sealed by melted paraffin. Thus each section was in an air-tight cell and could usually be preserved for some weeks without serious oxidation.

All the sodium-gold alloys were photographed by means of a Crookes' tube excited by a Ruhmkorff coil giving a 6-inch spark, the exposure varying from 5 to 30 minutes, according to the amount of gold present. The photographs 1 to 5 give the results of passing the Röntgen rays through sodium-gold.

Number 1 was a photograph from an alloy containing 3 per cent. of gold. It will be seen that the solid alloy is very far from being homogeneous, the bulk of the photograph consisting of light-coloured masses, strongly suggesting rectangular crystallisation, whilst the spaces between are filled with a much darker substance. Remembering that the photograph is a positive, we see that the larger and lighter part corresponds to a transparent substance which must therefore be mainly or entirely sodium, whilst the small quantity of dark interstitial matter

must, from its opacity, contain all or nearly all the gold. As the photograph was produced by a shadow, the thickness of the plate of alloy appears to have somewhat blurred the outline of the crystalline forms.

We here appear to be dealing with a process of solidification very similar to that of case *a* above referred to, a large amount of the solvent, in this case sodium, solidifying during the first stage of the cooling and leaving all the gold in a concentrated solution between the interstices of the crystals. During the second stage of the freezing, this eutectic alloy itself solidifies.

Figures 2 and 3 represent a similar phenomenon in the case of an alloy containing 10 per cent. of gold. The alloys were prepared in the same way but the sections cut were thinner, a fact which may account for the greater sharpness in the photographs. The opaque eutectic alloy necessarily occupies a larger space, but the contrast between the transparency of the crystals and the background is so strong that we are forced to the conclusion that the crystals of sodium contain but little, if any, gold. If we did not know from other grounds that the solvent sodium begins to solidify in these alloys before the gold, we could infer this from the straightness of the crystal lines, which in the photographs often exceed a centimetre in length. Both the transverse and longitudinal sections of this alloy show a system of interlacing lines; we are disposed to think, however, that these indicate the existence of plates of sodium standing at right angles to the plane of the section, as this is the only structure that would account for so great a difference of transparency. If this view is correct, the alloy must possess a remarkable cellular structure somewhat similar to that which has been thought to exist in certain kinds of steel. We may mention that, when after some months we removed the sections from their aluminium cells, it was noticed that the slight oxidation of the surface had produced a pattern resembling that of the photographs.

Figure 4 is a photograph through an alloy containing more than 23 per cent. of gold. It was made by adding excess of gold to sodium at a temperature above  $150^{\circ}$ , and then slowly cooling as before. The photograph shows that the process of solidification resembles that of case *b*, for the large transparent crystals of sodium are absent, and we have instead a network of extremely opaque needles which consist of almost pure gold. These lie in a finely-grained matrix which must be the eutectic alloy containing nearly all the sodium and a portion of the gold.

If an alloy such as No. 4 is thrown into alcohol, the sodium is removed and the gold is left as a felted mass of crystalline needles. The needles, which are often 3 millimetres or more in length, appear to be square in section. They are so entirely different in character

from the original gold used in making the alloy, that there can be no doubt of the gold having been completely in solution in the sodium. The gold used in making the alloy was prepared by precipitation with sulphur dioxide. Its crystals are very minute, but appear to be cubes or octahedra, needles being rarely or never present in it. In numerous analyses of the needles after removal of the excess of sodium by alcohol, we invariably found from 2 to 3 per cent. of sodium; to remove this sodium, it was necessary to ignite the crystals at a red heat and then extract for some time with water or alcohol. Thus it would seem that the substance of the needles contains a small amount of sodium.

Fig. 5 gives the result of photographing through the pure eutectic alloy. A transverse section was cut through the upper part of the same cylinder of alloy as that which furnished No. 4, the latter being cut from the middle of the cylinder. In 5 we see that the large black needles so conspicuous in 4 are almost absent, the reason being that as the gold began to crystallise from the fluid alloy it gradually sank towards the bottom, leaving a supernatant liquid of the composition of the eutectic alloy. In further confirmation of this, we found that a section cut from near the base of the cylinder was much richer in the gold needles than even section 4. In section 5, a few large crystals of sodium and of gold can still be seen, but the bulk of the alloy is much more uniform than in the other sections. Several attempts were made to prepare the eutectic alloy by weighing out gold and sodium in the exact eutectic proportion and heating the mixture in a sealed vacuum tube, but in most cases the photographs showed some large crystals of gold and sodium on a granular ground like that of No. 5. These photographs are of some interest, as the large crystals in what should be an eutectic alloy perhaps indicate supersaturation on the part of one or both metals, followed by rapid crystallisation. To save expense, however, No. 5 is the only case of an eutectic alloy reproduced in the paper.

The photographs show that the roughly uniform groundwork is, even in an eutectic alloy, not really homogeneous. Most probably, the gold and sodium separate side by side and simultaneously in very small crystals, although as the photographs admit of but little magnification, it is impossible to make out the separate crystals of the eutectic groundwork in such a section as No. 5. Osmond has, however, shown by a microscopic examination with a high power, that the eutectic alloy of silver and copper consists of white and red crystals; thus it is probable that eutectic alloys are as much conglomerates as the majority of other alloys, differing from them by the fineness of their grain and the greater uniformity of their composition.



*Gold-Aluminium Alloys.*

Aluminium is nearly as transparent as sodium, and it is known that gold dissolves freely in aluminium; alloys of these two metals were therefore the next selected for examination. The discovery by Professor Roberts-Austen of the chemical compound  $\text{AuAl}_2$  formed by these two metals when melted together, and the great stability of this compound (Trans., 1894, 65, p. 75) give an especial interest to this group of alloys. The alloys were made in a small Fletcher's blast furnace and slowly cooled in the manner described in the introduction and the appendix.

Two alloys containing 5 and 20 per cent. of gold respectively were made and cooled simultaneously.

The 5 per cent. alloy of figure 6 shows the structure of an unsaturated solution of gold in aluminium, for the aluminium has crystallised first in transparent lines which are so straight that they must have been formed at an early stage of the freezing. The dark basis, as before, represents the finely grained eutectic alloy. From the method of making the alloy, we are convinced that it was quite homogeneous when fluid, but the photographs show that, as the result of slow cooling, there has been a distinct concentration of the gold towards the central portions of the ingot, which, of course, remained hot longest. The rectangular character of the aluminium crystallisation is even more marked than that of the sodium in the alloys containing that metal. Sections 6 and 7 are vertical sections through the upper and lower halves respectively of the cylinder of alloy, and section 8 is a horizontal one through the middle of the cylinder. Section 7 was inverted.

Fig. 9 is the photograph of a horizontal section near the bottom of an alloy containing 11 per cent. of gold. It will be noticed that whilst the bulk of the photograph is a mosaic of light and dark probably corresponding to the eutectic alloy, a few intensely opaque crystals are visible near the edge of the section. A careful examination of the polished surface of the alloy itself, with the aid of a lens, reveals these crystals as purple markings. They are, therefore, Roberts-Austen's alloy,  $\text{AuAl}_2$ . From the small number of these crystals, we may conclude that the aluminium was not much more than saturated with this substance when the eutectic temperature was reached. Cryoscopic experiments have shown us that the eutectic alloy of gold and aluminium contains about 7.1 per cent. of gold, and an analysis of the upper middle part of the 20 per cent. gold alloy shows that this part contained 7.4 per cent. Au.

Although these photographs do not prove the point, we have reason



to think that none of the gold is uncombined, and that the eutectic alloy when solid is a finely grained mixture of crystals of aluminium and of  $\text{AuAl}_2$ . The outline of the opaque crystals strongly reminds one of those of potassium iodide. In Figs. 10 and 11 we have photographs of an alloy containing 20 per cent. of gold. Here, on account of the slowness of the cooling, the precipitated compound settles to the bottom as it forms, the upper part of the cylinder showing the coarsely mottled eutectic alloy, which is evidently far from being homogeneous, and the lower part affording an excellent picture of the crystals of the compound. In the negative of Fig. 10, some of the dark crystals appear to be octahedral, whilst in that of Fig. 11, which is a horizontal section near the bottom of the same cylinder, many appear to be cubical. A naked-eye examination of the surface of the section from which Fig. 10 is taken shows the brilliant purple of the compound.

We think that a careful examination of the upper part of Fig. 10, shows very well how completely heterogeneous an eutectic alloy may be, and that the fineness or coarseness of its grain is a mere function of the rate of cooling.

A striking contrast to these cases of slow cooling is presented by Fig. 12, which is the photograph of the same 20 per cent. gold alloy, but of a portion which has been quickly cooled by pouring on to a stone slab. It will be seen that the massive crystals are absent but that the whole alloy is full of minute black rods and rectangular crosses. These photographs illustrate very clearly the differences in structure that may exist between the same alloy when rapidly or when slowly cooled, and it is obvious that the mechanical properties would differ in a corresponding manner. Fig. 12A is a section of the quickly cooled 5 per cent. gold alloy; it will be seen to have a very uniform grain.

#### *Copper-Aluminium Alloys.*

Figs. 13 to 16 are photographs of copper-aluminium alloys taken in the same manner as the preceding.

An alloy containing 5 per cent. of copper is shown in Fig. 13. Here the long straight lines of the aluminium crystals resemble those seen in the gold-aluminium alloy number 6, and this might be expected, as they were formed under very similar conditions in the two cases. The darker eutectic alloy is, however, more uniformly distributed in the copper than in the gold alloy.

In Fig. 14, we have a horizontal section through the middle of a cylinder containing rather more than 14 per cent. of copper; several very perfect crosses of aluminium will be seen in this section, with a fern-like crystallisation starting from their arms. The dark eutectic alloy is here concentrated in one part of the section.

Figs. 15 and 16 are from an alloy containing 25 per cent. of copper. The aluminium crystals are smaller and have a more fern-like appearance, and the mother substance, of course, occupies more space. In 16, which is a vertical section, we see, in addition, a few very opaque needles, which must be either copper or a compound of copper and aluminium.

The 50 per cent. copper alloy is so brittle that we have as yet failed in obtaining sections thin enough to be transparent.

### *Silver-Aluminium Alloys.*

We have examined a number of slowly-cooled silver-aluminium alloys, but with the exception of the alloy  $\text{AgAl}_4$ , of Figs. 17, 18, and 19, we have not obtained as yet details in the X-ray photographs distinct enough for reproduction. Fig. 17 is a horizontal section, and 18 and 19 are vertical sections.

Slowly-cooled silver-zinc alloys, although the polished surfaces show abundant detail when examined by the naked eye or with a lens, show no detail in the photographs. The same is true of zinc-gold alloys.

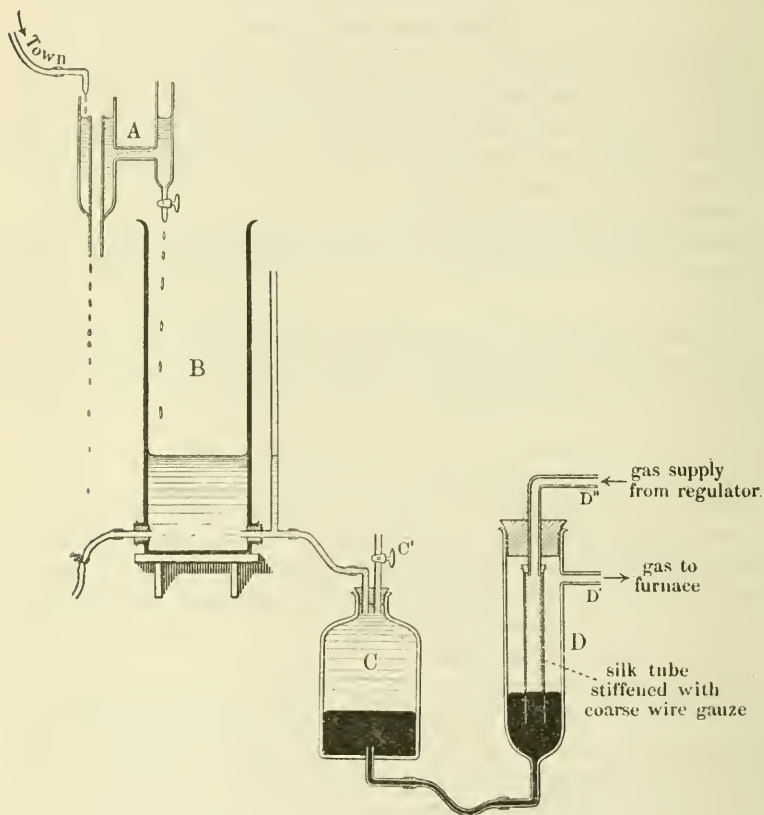
We have obtained very fine photographs from alloys of aluminium with either antimony, nickel, or platinum. We hope to discuss and reproduce these in a continuation of this paper.

### *Method of Cooling.*

In order to produce the very slow cooling required to make the alloys give the maximum separation, it was necessary to devise a special arrangement for slowly and continuously cutting off the gas from the furnace. The apparatus for this purpose is represented in the accompanying sketch, p. 722 (not drawn to scale); it is seen to consist essentially of four parts.

The constant level water dropper, *A*, worked very steadily, and obviated the difficulty caused by small gas bubbles collecting in the tap, and so stopping the flow of water. By measuring the water which drops into a graduated cylinder for one minute, and knowing the capacity of the cylinder *B*, we can ascertain the rate at which the gas will be cut off. The zinc cylinder *B* is about 4 feet high and 10 inches in diameter, and holds some 55 litres; it is provided with a water gauge and emptying tube as shown in the diagram; it has also an overflow at the top. This zinc cylinder is connected by a rubber tube with the narrow necked bottle *C*, of about 250 c.c. capacity. This bottle, which should be rather wide in proportion to its height, has a hole drilled in its bottom, into which a glass tube is cemented. The tap *C'* is for the purpose of getting rid of air bubbles which are liable

to collect in *C*. Joined to *C* by a thick-walled rubber tube is the gas cut-off *D*; the tube *D* is 15 cm. long and 2.5 cm. wide, and it contains an inner tube made of fifteen layers of fine silk wound round the outside of a cylinder of coarse iron wire gauze in order to give it rigidity. The silk tube is open at its lower end, and is fastened at its upper end to the glass tube *D'*, by the aid of cement. With a gas pressure of about 1 inch of water, the silk tube, even with 15 layers, allows more gas to pass than



is required to keep a Fletcher's draught furnace (No. 363) up to a temperature of the melting point of silver. This difficulty was got over by entirely coating the silk tube with a very viscous shellac, except for a line about 2 mm. wide running from top to bottom of the silk. It will be seen by the aid of the diagram that, as the water drips into *B*, the pressure on the surface of the mercury in *C* slowly and steadily increases, thus causing the mercury to flood the tube *D*

## PLATE I.

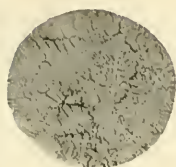


FIG 1

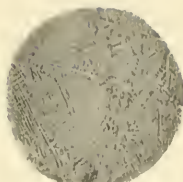


FIG 2



FIG 3

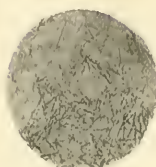


FIG 4



FIG 5



FIG 6

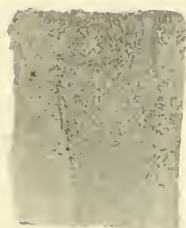


FIG 7

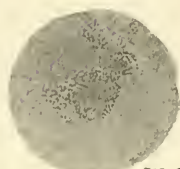


FIG 8

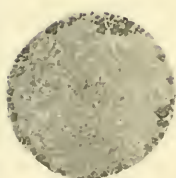


FIG 9



FIG 10

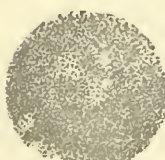


FIG 11



FIG 12

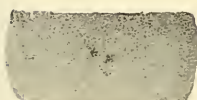


FIG 12 A

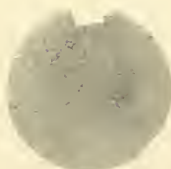


FIG 13

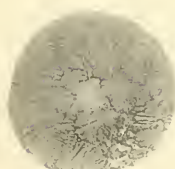


FIG 14

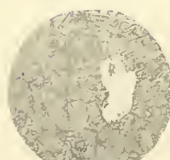


FIG 15



FIG 16



FIG 17

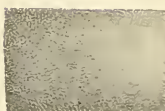


FIG 18



FIG 19





both inside and out, and hence to gradually cut off the escape of gas through the unvarnished portion.

Such a cut-off is useless unless the gas pressure is kept constant. The pressure regulator we have used was designed by Mr. Horace Darwin, and supplied by the Cambridge Scientific Instrument Company. Careful measurements have shown that this regulator controls the very great variations of gas pressure we have in Cambridge, passing, as they do, from a minimum of about  $1\frac{3}{4}$  inches to a maximum of about 3 inches; it also overcomes the changes of pressure produced by conducting other furnace operations simultaneously in the laboratory. The regulator has the additional advantage that it can be loaded with weights so as to deliver gas to the burner at any desired pressure up to the minimum of the town supply. In order to obtain the greatest possible steadiness during the cooling, we place a large clay crucible in the furnace, and set within it two or three small salamander cylinders of about 22 c.c. capacity, the interstices between the cylinders being filled in with sand. The furnace is heated to the highest temperature required, and the water dropper and cut-off set working. The alloys are then melted and thoroughly stirred in a blast furnace, poured into the salamander cylinders, and allowed to cool down; this process of cooling usually occupies from 40 to 50 hours. When dealing with alloys which melt at a high temperature we can, by aid of a bye-pass, allow sufficient gas to pass direct to the furnace to keep it at the lowest temperature required, the cut-off thus becoming more efficient.

SIDNEY COLLEGE,  
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## LXXIX.—*Additive Compounds of Organic Bases and Ethereal Salts of Unsaturated Acids.*

By S. RUHEMANN, Ph.D., M.A., and K. C. BROWNING, B.A.

WHILST engaged in the further study of the compounds obtained by the interaction of the sodium derivative of ethylic oxalacetate and ethylic chlorofumarate (Ruhemann and Hemmy, Trans., 1897, 71, 334) with the view of determining their constitution, we made certain observations which form the subject of this communication; especially in relation to the substance forming blue salts with alkalis. This had been provisionally regarded as triethylic anhydro-oxalaconitate,  $\text{COOC}_2\text{H}_5 \cdot \text{C} \equiv \text{C} \cdot \text{COOC}_2\text{H}_5$ , and its formation was attributed to the condensation of 2 mols. of ethylic oxalacetate, the ethylic

chlorofumarate being supposed to take no part in the reaction. This assumption was found to be correct, because it was ascertained that the same product was formed on digesting ethylic oxalacetate with sodium ethoxide, the yield, however, is very small as in the former case. In attempting to prepare this compound by the condensation of ethylic oxalacetate with ethylic aconitate, we observed that piperidine unites with ethylic aconitate, forming an oil of basic character. Similar additive products are also obtained by using other ethereal salts of unsaturated acids; we have, up to the present, also prepared corresponding compounds from ethylic fumarate and ethylic citraconate. We find, moreover, that piperidine not only combines with the ethereal salts of acids containing an ethylene linking, but also with those which have a triple bond. As examples of the latter, we have chosen ethylic phenylpropiolate, and have made the interesting observation that, in this case, the union with piperidine is accompanied by a strong evolution of heat. These additive compounds can be distilled under diminished pressure without undergoing decomposition, they are not affected by dilute potash, and with hydrogen chloride form salts which are extremely soluble in water.

These substances differ in their properties from the compound which is formed by mixing an ice cold ethereal solution of ethylic dicarboxylglutaconate with aniline (Guthzeit, *Ber.*, 1897, 30, 1757). Guthzeit regards this compound as ethylic anilidodicarboxylglutarate, whilst it might have been expected that a substance with such acid properties as ethylic dicarboxylglutaconate would yield with aniline a salt similar to those which it forms with alkalis, with guanidine, and with diethylamine (see Ruhemann and Hemmy, *Ber.*, 1897, 30, 2022).

#### *Ethylic Piperidylsuccinate.*

Ethylic fumarate and piperidine interact with development of heat. A mixture of the ethereal salt and the base in equivalent quantities is digested on the water bath for 8—10 hours, and the oily product subjected to fractional distillation under reduced pressure; the largest fraction, that which boils at 162—164°, on redistillation, distils at 159° under a pressure of 10 mm. The analysis of this oil corresponds with the formula  $C_5H_{10}N \cdot CH \cdot COOC_2H_5$ .

$$\begin{array}{c} | \\ CH_2 \cdot COOC_2H_5 \end{array}$$

0.2406 gave 0.5354  $CO_2$  and 0.1963  $H_2O$ .  $C = 60.68$ ;  $H = 9.06$ .

0.2260 „ 11 c.c. nitrogen at 20° and 765 mm.  $N = 5.59$ .

$C_{13}H_{23}NO_4$  requires  $C = 60.70$ ;  $H = 8.94$ ;  $N = 5.49$  per cent.

Ethylic piperidylsuccinate, freshly distilled, is a colourless oil having a density  $d_{18^\circ/18^\circ} = 1.0469$ , and a slight odour of piperidine,

which becomes yellow after standing for a day. It is readily soluble in alcohol and ether, but insoluble in water. On passing hydrogen chloride into the solution of the ethereal salt in ether dried over sodium, a white precipitate of the hydrochloride is thrown down in colourless prisms; this is very soluble in water and in alcohol, but insoluble in ether, it begins to soften at  $135^{\circ}$ , and melts at  $140^{\circ}$  to a clear liquid, which, on cooling, solidifies again after a time. The percentage of chlorine, as determined by precipitating the aqueous solution of the substance with silver nitrate, corresponds with the formula  $C_{13}H_{23}NO_4 \cdot HCl$ .

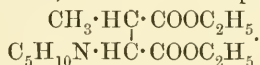
0.3563 gave 0.1743 AgCl.  $Cl = 12.10$ .

$C_{13}H_{23}NO_4 \cdot HCl$  requires  $Cl = 12.095$  per cent.

Potash added to the aqueous solution of the hydrochloride precipitates the basic ethereal salt.

*Ethylic Piperidylpyrotartrate.*

This is formed in the same manner as the above, by digesting a mixture of piperidine with ethylic citraconate on the water bath, and fractionating the product. One redistillation of the fraction of higher boiling point suffices to obtain a pure compound boiling at  $163\text{--}164^{\circ}$  under a pressure of 10 mm., and of the composition



0.2341 gave 0.5305  $CO_2$  and 0.1945  $H_2O$ .  $C = 61.80$ ;  $H = 9.23$

0.2917 „ 13.5 c.c. of moist nitrogen at  $21^{\circ}$  and 756 mm.  $N = 5.24$ .

$C_{14}H_{25}NO_4$  requires  $C = 61.99$ ;  $H = 9.22$ ;  $N = 5.17$  per cent.

Ethylic piperidylpyrotartrate is also colourless when freshly distilled, but becomes yellow after some time; its density is  $d_{18^{\circ}/18^{\circ}} = 1.0333$ .

Hydrogen chloride, on being passed into a solution of the ethereal salt in dry ether, throws down a white, crystalline solid which does not melt sharply at  $115^{\circ}$ , dissolves in water with the greatest ease, and is insoluble in ether.

0.4067, dried in a vacuum, gave 0.1910 AgCl.  $Cl = 11.61$ .

$C_{14}H_{25}NO_4 \cdot HCl$  requires  $Cl = 11.54$  per cent.

*Ethylic Piperidyltricarballylate.*

The union of piperidine with ethylic aconitate takes place to a small extent on mixing the two, and is accompanied by a slight evolution of

heat and a yellow coloration of the mixture. A satisfactory yield of the additive compound, however, is obtained by heating the mixture on the water bath for a day; it can be isolated by repeated distillation in a vacuum, and boils at  $201\text{--}202^\circ$  under a pressure of 10 mm.

The analysis corresponds with the formula for ethylic piperidyltricarballylate,  $(\text{COOC}_2\text{H}_5 \cdot \text{CH}_2)_2\text{C}(\text{N} \cdot \text{C}_5\text{H}_{10}) \cdot \text{COOC}_2\text{H}_5$ .

0.2479 gave 0.5435  $\text{CO}_2$  and 0.1880  $\text{H}_2\text{O}$ .  $\text{C} = 59.79$ ;  $\text{H} = 8.45$ .

0.2434 „ 0.5394  $\text{CO}_2$  „ 0.1840  $\text{H}_2\text{O}$ .  $\text{C} = 59.32$ ;  $\text{H} = 8.40$ .

0.2416 „ 0.5264  $\text{CO}_2$  „ 0.1849  $\text{H}_2\text{O}$ .  $\text{C} = 59.42$ ;  $\text{H} = 8.45$ .

0.2707 „ 10 c.c. nitrogen at  $22^\circ$  and 759 mm.  $\text{N} = 4.17$ .

$\text{C}_{17}\text{H}_{20}\text{NO}_6$  requires  $\text{C} = 59.47$ ;  $\text{H} = 8.45$ ;  $\text{N} = 4.08$  per cent.

The additive compound is a pale yellow oil with green fluorescence, and on standing for some days becomes red; its density is  $d_{20^\circ/20^\circ} = 1.084$ .

Hydrogen chloride, on being passed into a solution of the ethereal salt in dry ether precipitates, as in the former cases, a salt in colourless needles which, dried in a vacuum over potash and sulphuric acid, melts, not sharply, at  $110^\circ$ .

A chlorine determination gave the following result.

0.3368 gave 0.1271  $\text{AgCl}$ .  $\text{Cl} = 9.34$ .

$\text{C}_{17}\text{H}_{20}\text{NO}_6 \cdot \text{HCl}$  requires  $\text{Cl} = 9.35$  per cent.

On adding potash to an aqueous solution of the hydrochloride, an oil is precipitated, which, on examination, was found to be unaltered ethylic piperidyltricarballylate; decomposition of the additive compound into piperidine and aconitic acid takes place, however, on boiling it with concentrated aqueous potash.

*Ethylic Piperidylcinnamate*,  $\text{C}_6\text{H}_5 \cdot \text{CH} : \text{C}(\text{C}_5\text{NH}_{10}) \cdot \text{COOC}_2\text{H}_5$ .

The addition of piperidine to ethylic phenylpropiolate, as already mentioned, is accompanied by great evolution of heat, and the dark-coloured product, on fractionation under diminished pressure, yields a viscous yellow oil which boils at  $220\text{--}221^\circ$  under a pressure of 11 mm., and has a density  $d_{18^\circ/18^\circ} = 1.0730$ .

0.2181 gave 0.5948  $\text{CO}_2$  and 0.1625  $\text{H}_2\text{O}$ .  $\text{C} = 74.37$ ;  $\text{H} = 8.27$ .

$\text{C}_{16}\text{H}_{21}\text{NO}_2$  requires  $\text{C} = 74.13$ ;  $\text{H} = 8.11$  per cent.

Ethylic piperidylcinnamate, like the other additive compounds, yields a hydrochloride; this separates as a yellow precipitate on passing hydrogen chloride into the ethereal solution of the oil, but on filtration becomes pasty.

We are engaged in the study of the action of other organic bases on the ethereal salts of unsaturated acids, and hope to be able to publish the result in a short time.

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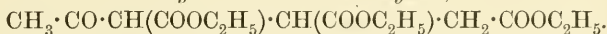
### LXXX.—*Formation of Ethereal Salts of $\beta$ -Ketonic Acids*

By S. RUEHMANN, Ph.D., M.A., and K. C. BROWNING, B.A.

SINCE Michael (*J. pr. Chem.*, 1887, 35, 349) made the interesting observation that the ethereal salts of the sodium derivatives of ethylic acetoacetate and ethylic malonate have the property of uniting with the ethereal salts of unsaturated acids, this reaction has been applied, especially by Auwers (*Ber.*, 1891, 24, 307, 2887) to ethylic malonate, but it has scarcely been used for the production of ethereal salts of  $\beta$ -ketonic acids. In the course of our researches on this class of compounds, we have prepared several members of the group in this way.

The experiments were carried out as follows. The ethereal salt of the  $\beta$ -ketonic acid was added to an equivalent quantity of dry sodium ethoxide suspended in ether which was free from water and alcohol, and the solution thus obtained mixed with the corresponding weight of the ethereal salt of the unsaturated acid. The mixture, after 2 to 3 days, was acidified with dilute sulphuric acid, the ethereal layer shaken with sodium carbonate, and the oil remaining after removal of the ether fractionated under diminished pressure.

#### *Ethylic $\alpha$ -Acetotricarballylate,*



On adding ethylic fumarate to ethylic sodioacetoacetate, heat is evolved; the ethereal solution, after being allowed to stand overnight, is treated in the manner mentioned above. The oily residue left on evaporating the ether, when fractionated under diminished pressure, yields 75 per cent. of the theoretical quantity of ethylic  $\alpha$ -acetotricarballylate, boiling at 187–188° under a pressure of 11 mm.

0.2538 gave 0.5154  $\text{CO}_2$  and 0.1614  $\text{H}_2\text{O}$ .  $\text{C} = 55.38$ ;  $\text{H} = 7.06$ .

$\text{C}_{14}\text{H}_{22}\text{O}_7$  requires  $\text{C} = 55.26$ ;  $\text{H} = 7.23$  per cent.

This ethereal salt had already been obtained by Emery (*Ber.*, 1890, 23, 3757) by the interaction of ethylic sodioacetoacetate and ethylic monochlorosuccinate, and the boiling point found was 175° under a pressure of 9 mm.



Ferric chloride gives a red violet coloration with an alcoholic solution of the ethereal salt. Concentrated aqueous ammonia dissolves ethylic  $\alpha$ -acetotricarballylate if left in contact with it for a short time, and the solution after 3 to 4 days deposits crystals, whilst the ammoniacal liquor turns red; these crystals dissolve in boiling water, and, on cooling, are deposited in colourless prisms, which become darkened, and melt at  $248^\circ$  with evolution of gas. Its aqueous solution gives a violet coloration with ferric chloride, this indicating that the substance still contains the grouping of acetoacetic acid. This conclusion is, moreover, supported by the following analytical data, which correspond with the formula



for the amide of acetotricarballylic acid.

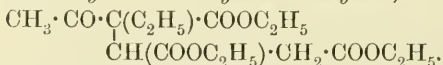
0.2301 gave 0.3771  $\text{CO}_2$  and 0.1280  $\text{H}_2\text{O}$ .  $\text{C} = 44.69$ ;  $\text{H} = 6.18$ .

0.1428 „ 25 c.c. nitrogen at  $25^\circ$  and 760 mm. ;  $\text{N} = 19.53$ .

$\text{C}_8\text{H}_{13}\text{N}_3\text{O}_4$  requires  $\text{C} = 44.65$ .  $\text{H} = 6.05$ ;  $\text{N} = 19.53$  per cent.

The yield of the amide is very small; the greater part of the ethereal salt being decomposed by the ammonia and transformed into a dark tarry substance, which is left on evaporating the ammoniacal mother liquor.

*Ethylic Acetoethyltricarballylate,*

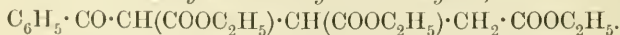


Like ethylic sodioacetoacetate, the sodium derivatives of the mono-substitution products of the ethereal salt combine with ethereal salts of unsaturated acids. We have chosen ethylic acetoacetate and, proceeding as before, have found that, in the presence of sodium ethoxide, it combines with ethylic fumarate. After repeated fractional distillation, the product, ethylic acetoethyltricarballylate, is obtained as a colourless oil which boils at  $194$ — $196^\circ$  under a pressure of 9 mm., and has a density  $d_{19^\circ/19^\circ} = 1.0996$ .

0.2244 gave 0.4780  $\text{CO}_2$  and 0.1598  $\text{H}_2\text{O}$ .  $\text{C} = 58.10$ ;  $\text{H} = 7.91$ .

$\text{C}_{16}\text{H}_{26}\text{O}_7$  requires  $\text{C} = 58.18$ ;  $\text{H} = 7.88$  per cent.

*Ethylic  $\alpha$ -Benzoyltricarballylate,*



The reaction between ethylic fumarate and the sodium derivative of ethylic benzoylacetate is complete after 2 days; the ethereal solution of the product is treated first with dilute sulphuric acid and then with sodium carbonate, and on removal of the ether leaves a viscous, yellow oil which exhibits a green fluorescence, and distils at  $244$ — $245^\circ$

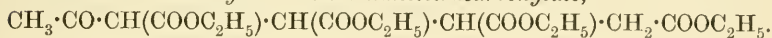
under a pressure of 10 mm. On analysis, the following numbers were obtained.

0.2331 gave 0.5370  $\text{CO}_2$  and 0.1345  $\text{H}_2\text{O}$ .  $\text{C} = 62.82$ ;  $\text{H} = 6.41$ .

$\text{C}_{19}\text{H}_{24}\text{O}_7$  requires  $\text{C} = 62.63$ ;  $\text{H} = 6.59$  per cent.

The same compound had previously been prepared by Emery (*J. pr. Chem.*, 1896, 53, 312) by the action of ethylic chlorosuccinate on ethylic sodiobenzoylacetate, and he found the boiling point to be  $250^\circ$  under a pressure of 16 mm.

*Ethylic  $\alpha$ -Acetobutanetettracarboxylate,*



Ethylic aconitate combines with the sodium derivative of ethylic acetoacetate with the same readiness as ethylic fumarate; this is effected by adding to a solution of ethylic acetoacetate in dry ether the equivalent quantity of sodium ethoxide, dried in a vacuum at  $180^\circ$ , and then, as soon as the latter has dissolved, the calculated amount of ethylic aconitate. The mixture is left for 3 days, and the red ethereal solution thus obtained subjected to the treatment already described. The oily residue left on distilling off the ether, on being fractionated, boils at  $222\text{--}223^\circ$  under a pressure of 10 mm.

0.2242 gave 0.4577  $\text{CO}_2$  and 0.1436  $\text{H}_2\text{O}$ .  $\text{C} = 55.67$ ;  $\text{H} = 7.11$ .

$\text{C}_{18}\text{H}_{28}\text{O}_9$  requires  $\text{C} = 55.67$ ;  $\text{H} = 7.21$  per cent.

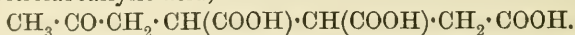
Ethylic  $\alpha$ -acetobutanetettracarboxylate is a pale yellow oil with a green fluorescence, and has a density  $d_{26^\circ/26^\circ} = 1.1462$ .

Concentrated aqueous ammonia dissolves the ethereal salt in the course of some hours, the solution becoming red, and after 3—4 days it deposits a solid which is obtained in colourless plates on crystallisation from boiling water; it decomposes at about  $268^\circ$  without melting. The yield of this substance was so small that, although 5 grams of the ethereal salt had been used, it did not suffice for establishing its composition by an analysis. There can, however, be no doubt that it is the amide of acetobutanetettracarboxylic acid. The ammoniacal filtrate from the solid is strongly fluorescent, and on evaporation leaves a dark, tarry residue.

*Acetonyltricarballic Acid.*

The hydrolysis of acetobutanetettracarboxylate is best effected by boiling with hydrochloric acid (diluted with an equal volume of water) in a reflux apparatus. After 3 hours heating, the oil disappears, and on evaporating the solution on the water bath, an oily residue is left which slowly solidifies to a hard, amorphous mass. This becomes

liquid at  $100^\circ$  and sets again to a solid after some days; it is only slightly soluble in ether, but readily in water and in alcohol, and separates as an oil which slowly solidifies, but not until the solvent has evaporated. Analysis of the product dried at  $100^\circ$  indicates that it is  $\alpha$ -acetonyltricarballic acid,



0.2357 gave 0.4010  $\text{CO}_2$  and 0.1130  $\text{H}_2\text{O}$ .  $\text{C} = 46.40$ ;  $\text{H} = 5.32$ .

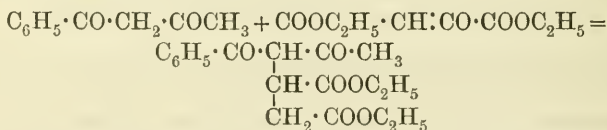
$\text{C}_9\text{H}_{12}\text{O}_7$  requires  $\text{C} = 46.55$ ;  $\text{H} = 5.17$  per cent.

The composition of the acid is, moreover, supported by the analysis of the silver salt; on adding silver nitrate to an aqueous solution of the acid neutralised with ammonia, this salt is thrown down as a white precipitate which is somewhat soluble in cold water.

0.2770, dried at  $100^\circ$ , gave 0.1628 Ag.  $\text{Ag} = 58.77$ .

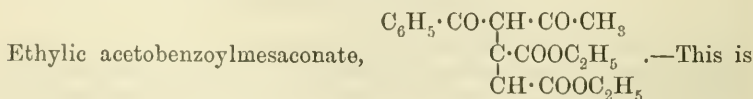
$\text{C}_9\text{H}_{11}\text{AgO}_7$  requires  $\text{Ag} = 58.59$  per cent.

The readiness with which the sodium derivatives of ethereal salts of  $\beta$ -ketonic acids unite with the ethereal salts of unsaturated acids induced us to examine whether  $\beta$ -diketones in the presence of sodium ethoxide would behave in a similar way. For this purpose, we chose benzoylacetone and ethylic fumarate, in the hope that a reaction would take place in accordance with the equation



On making the experiment in the same manner as described in the former cases, it was found, however, that, after allowing the mixture, in presence of sodium ethoxide and diluted with dry ether, to remain for 5 days, the larger portion of the diketone and ethereal salt remained unaltered, and that only a small quantity of an oil of high boiling point was formed, which, moreover, contained a higher percentage of carbon than the required compound.

The corresponding ethereal salt of the unsaturated diketonic acid, on the other hand, is readily formed by the interaction of sodium-benzoylacetone on ethylic chlorofumarate.



formed by adding 20 grams of benzoylacetone to a solution of 2.85 grams of sodium in 100 c.c. of absolute alcohol, and then 25.5 grams

of ethylic chlorofumarate. After 2 hours digestion on the water bath, the mixture ceases to be alkaline to litmus; the product is then poured into water, and the oil which separates extracted with ether. On evaporating the ether, an oil is left which distils at  $233\text{--}235^\circ$  under a pressure of 10 mm.; it is very viscous, of a yellow colour, and gives in alcoholic solution a wine-red coloration with ferric chloride.

0.3058 gave 0.7320  $\text{CO}_2$  and 0.1645  $\text{H}_2\text{O}$ .  $\text{C} = 65.26$ ;  $\text{H} = 5.97$ .

$\text{C}_{18}\text{H}_{20}\text{O}_6$  requires  $\text{C} = 65.06$ ;  $\text{H} = 6.02$  per cent.

We propose to continue this investigation, and to examine whether the union of ethereal salts of  $\beta$ -ketonic acids with those of unsaturated acids takes place under conditions similar to those of ethylic malonate and its homologues.

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### LXXXI.—*Disulphonic Acids of Toluene, of Ortho- and Para-toluidine, and of Ortho- and Para-chlorotoluene.*

By WILLIAM PALMER WYNNE, D.Sc., F.R.S., and JAMES BRUCE, B.Sc.,  
Assoc. R.S.M.

IN a previous paper by one of us (Trans., 1892, 61, 1078), an account was given of experiments undertaken with the object of determining the proportions in which parachlorotoluene-2- and -3-sulphonic acids ( $\text{Me} = 1$ ) occur in the product obtained in sulphonating parachlorotoluene with three times its weight of pure (100 per cent.) sulphuric acid at the temperature of a water bath. The process used was that of fractional crystallisation of the mixed barium salts obtained from the product, but the results were inconclusive and unsatisfactory. The 1:4:2-isomeride was recognised as being present in the less soluble fractions by converting them into the chlorides, from which a crystalline separation, representing about one-sixth of the whole, was obtained; this melted at  $18^\circ$  and gave an amide melting at  $139\text{--}140^\circ$ , which seemed to be identical with the 1:4:2-amide previously described by Heffter (*Annalen*, 1883, 221, 209). The greater part of the chloride was an uncrystallisable oil, and as an oily chloride was also obtained from the more soluble portions of the barium salt, with a corresponding amide melting at about  $120^\circ$ , the conclusion was drawn that "the 1:2:4-salt is present in the smaller quantity; in other words, that the chief product of



the action of sulphuric acid on parachlorotoluene is the 1:3:4-parachlorotoluenesulphonic acid."

This conclusion was not in harmony with that arrived at from a consideration of the results obtained by Hübner and Post (*Annalen*, 1873, 169, 6; compare Jennsen, *ibid.*, 1874, 172, 238; Pechmann, *ibid.*, 1874, 173, 208; Miller, *Trans.*, 1892, 61, 1026), and by Kornatzki (*Annalen*, 1883, 221, 191) on sulphonating parabromotoluene, as in this case the 1:4:2-isomeride must be the chief product. In consequence of this discrepancy, and because little was known of the derivatives of parachlorotoluene-3-sulphonic acid, it was stated that "the examination of the parachlorotoluenesulphonic acids is being continued with the object of isolating the two isomeric forms in a state of purity; parachlorotoluenesulphonic acids are also being prepared from the isomeric paratoluidinesulphonic acids for the purposes of comparison." A preliminary communication on this subject was made about three years ago (*Proc.*, 1895, 11, 152), and the present paper contains the results of the investigation, so far as we have been able to pursue it conjointly.

At the outset it is necessary to state that further investigation has shown that the statements contained in the second paragraph and in the last paragraph but one in the note in the Proceedings are erroneous. The "paratoluidinedisulphonic acids obtained by Richter from the 1:3:4- and the 1:2:4-paratoluidinemonosulphonic acids" are now shown to be not the "1:3:4:6- and 1:2:4:6-derivatives," but the 1:3:4:5- and 1:2:4:5-derivatives respectively. Also "the former," that is, the supposed 1:3:4:6-disulphonic acid, "by elimination of the  $\text{NH}_2$ -radicle, gives a toluenedisulphonic acid identical" not with that "obtained from the 1:2:5-orthotoluidinesulphonic acid by the xanthate method," but with the 1:3:5-derivative (*loc. cit.*, 153). Further the "1:2:6-toluenedisulphonic acid" obtained from the supposed "1:2:4:6-paratoluidinedisulphonic acid by eliminating the  $\text{NH}_2$ -radicle" is the 1:2:5-derivative, identical with that prepared from 1:2:5-orthotoluidinesulphonic acid by the xanthate method (*loc. cit.*, 154).

These errors, regrettable as they are, may perhaps serve to indicate the difficulty experienced in working with toluene- and chlorotoluenedisulphonic acids. In the case of naphthalene derivatives, the chlorides often have been found to be invaluable for the purpose of separating isomerides readily from one another (compare Armstrong and Wynne, *Proc.*, 1888, 4, 106; 1890, 6, 82). With toluene derivatives, however, it is different, as may be seen from the account of experiments made with the object of separating one of the isomerides from mixtures of the parachlorotoluene-2- and -3-sulphonic chlorides containing known proportions of the two; success in the preparation of definite chlorides



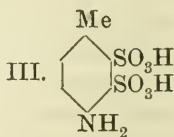
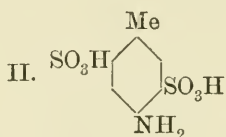
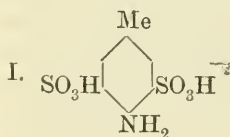
depends largely on the purity of the salts employed, or, in other words, on the efficiency of fractional crystallisation as a means of separating the constituents from a mixture of isomeric salts. Even when using pure salts, the crude chloride frequently was found to contain some oily, uncrystallisable substance, and in the case of impure salts the proportion of this oil occasionally became considerable, in consequence, no doubt, of the formation of a mixture of chlorides having a fusing point lower than that of any of its constituents. The sulphonic chlorides, as previously stated (*Trans.*, 1892, 61, 1074), are not converted simply into the corresponding halogen derivatives of toluene by distillation with phosphorus pentachloride, and in doubtful cases it was found that the anilides, which usually crystallise well, were best adapted for the purpose of characterising them.

A re-examination of the barium salt of the product obtained by sulphonating parachlorotoluene failed to give definite results, just as on the previous occasion, and although some 1 : 4 : 2-salt was separated from the least soluble fractions, no satisfactory evidence was forthcoming of the presence of the 1 : 4 : 3-salt in the most soluble portion. It became evident, therefore, that some other method for solving the problem had to be devised, and, in consequence, the disulphonic acids formed respectively from pure potassium 1 : 4 : 2- and 1 : 4 : 3-parachlorotoluenesulphonates were examined in order to ascertain whether further sulphonation would afford the desired means of obtaining information with respect to the proportions in which the isomerides exist in the mixture. Investigation showed (1) that each salt gave two isomeric disulphonic acids, of which one was formed from both salts, (2) that the mixed potassium disulphonates could be separated and their relative proportions estimated by fractional crystallisation, (3) that intramolecular change did not occur in the production of the disulphonic acids, and (4) that the mixture of potassium monosulphonates obtained from parachlorotoluene gave the three disulphonic acids in such proportions that it must have contained at least 86 per cent. of the 1 : 4 : 2-isomeride. This conclusion is the converse of that thought probable from the earlier experiments, and makes it evident that parachlorotoluene resembles parabromotoluene in yielding the 1 : 4 : 2-derivative as the chief product on sulphonation.

A knowledge of the constitution of these chlorotoluenedisulphonic acids was necessary both in elucidating the problem and in determining whether intramolecular change occurred during further sulphonation. The paratoluidinedisulphonic acids prepared and described by Richter (*Annalen*, 1885, 230, 314, 331) were utilised for this purpose, and the opportunity was taken to revise and extend the information given in his paper. Simultaneously, the disulphonic acid prepared from orthotoluidine-5-sulphonic acid by Nevile and Winther (*Trans.*,

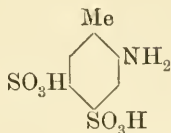
1882, 41, 421) and further examined by Hasse (*Annalen*, 1885, 230, 286), and that obtained from the isomeric orthotoluidine-4-sulphonic acid were investigated in connection with the examination of the disulphonic acids formed on sulphonating the corresponding orthochlorotoluenesulphonic acids. By eliminating the  $\text{NH}_2$ -radicle from the toluidinedisulphonic acids, toluenedisulphonic acids were obtained, and as these were of considerable importance in determining the constitution of the toluidine derivatives, three were prepared for purposes of comparison from the toluidinemonosulphonic acids by conversion into the mercaptans (or disulphides) and subsequent oxidation with potassium permanganate. The toluene-2:5- and -3:4-disulphonic acids were obtained by Klason in this way, using potassium sulphide (*Ber.*, 1887, 20, 350); we employed potassium xanthate for the purpose (Leuckart, *J. pr. Chem.*, 1890, [ii], 41, 179), but were unable to obtain a better yield than 20 per cent. of the theoretical amount under the most favourable conditions.

Among the results obtained in the course of the examination of the toluidinedisulphonic acids, reference may be made to the following. A revision of Hasse's work on Neville and Winther's orthotoluidine-3:5-disulphonic acid made it clear that he was in error in his description both of the derived bromotoluenedisulphonic acid and of the toluene-3:5-disulphonic acid. The correction in the latter case is of importance, because Richter, working in the same laboratory, was led to conclude from these erroneous results that the paratoluidinedisulphonic acid obtained from paratoluidine-3-sulphonic acid could not have the formula I,

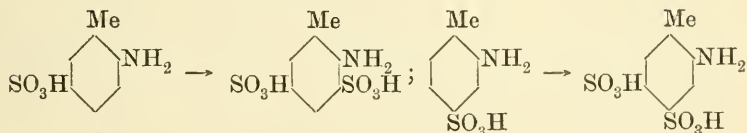


as the derived toluenedisulphonic acid differed from Hasse's compound, and, as a consequence, was thought to have the constitution represented either by II or III, between which his experiments did not enable him to decide. We have proved that toluene-3:5-disulphonic acid is obtained from both sources and agrees with Richter's description, so that his acid is represented by the first of the three formulæ. Richter prepared an isomeric disulphonic acid from paratoluidine-2-sulphonic acid, but only described its salts. Our experiments show that its constitution is represented by formula II, and that the derived toluene-2:5-disulphonic acid is identical with that prepared from orthotoluidine-5-sulphonic acid by the xanthate method.

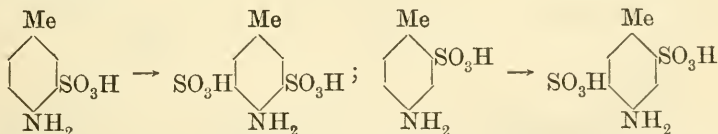
One disulphonic acid is obtained from orthotoluidine-4-sulphonic acid on further sulphonation, and its constitution is represented by the formula



This result is interesting, because it affords one of the rare instances of sulphonation proceeding in such a way that the entering group assumes a position contiguous to that of the  $\text{SO}_3\text{H}$ -radicle already present in the molecule. It is remarkable also from another point of view. Claus and Immel prepared the monosulphonic acid by the action of 50 per cent. anhydrosulphuric acid on orthotoluidine sulphate at  $0^\circ$ , whereas Nevile and Winther's orthotoluidine-5-sulphonic acid is obtained either when orthotoluidine sulphate is baked at about  $200^\circ$ , or when orthotoluidine (necessarily as sulphate) is heated at about the same temperature with ordinary sulphuric acid. It might be supposed, therefore, that Claus and Immel's acid would be the less stable of the two, and possibly would undergo more or less complete conversion into Nevile and Winther's acid during further sulphonation at a high temperature. But no evidence of any such change could be obtained, and that it does not occur seems clear from an inspection of the formulæ of the single disulphonic acid obtained from each of the acids respectively.



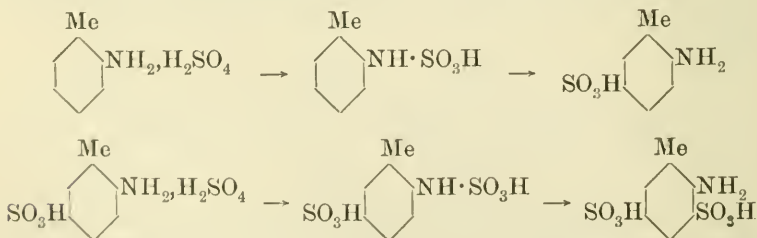
These results may be compared with those obtained from the paratoluidinesulphonic acids, each of which also gives rise to a single disulphonic acid.



It is a fair inference from these examples, that intramolecular change does not occur in the course of further sulphonation under the conditions employed. It is true that chlorosulphonic acid was the agent used in each instance, but Richter states that in the case of the paratoluidinesulphonic acids either this acid or fuming sulphuric acid

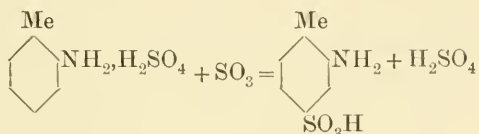
may be employed; moreover, he describes only one disulphonic acid from each, whereas both must have been produced if the 1:4:3- changed partly into the 1:4:2-isomeride, or *vice versa*, prior to or during further sulphonation, and adds that, by partial hydrolysis of each of the disulphonic acids, he obtained the respective monosulphonic acid from which it had been prepared. On these grounds, we are unable to accept, without further evidence, Pechmann's statement that when either paratoluidine-2- or -3-sulphonic acid (5 grams) is heated with twice its weight of fuming sulphuric acid at 180–200° during 20 minutes, it is converted into a mixture of the 1:4:2-isomeride (3 grams), 1:4:3-acid (1 gram), and a disulphonic acid (*Annalen*, 1874, 173, 195). Pechmann's paper is concerned with the 1:4:3-acid, and contains no reference to the method by which the presence of 1:4:2-acid was recognised and placed beyond doubt, although a mode of separating the constituents of the mixture is described. If, as Pechmann states, paratoluidine yields a mixture of the same three acids when heated in a dish with twice its weight of fuming sulphuric acid at 180°, it seems remarkable that neither Nevile and Winther nor ourselves have detected the presence of the 1:4:2-isomeride in the product obtained from paratoluidine sulphate.

The mode in which sulphonation occurs in benzenoid amines is a problem which has attracted much attention, but still awaits a complete solution. With orthotoluidine and paratoluidine and their monosulphonic acids, it is evident from what has just been said that, with the exception of Claus and Immel's acid, the entering  $\text{SO}_3\text{H}$ -radicle assumes the para-, or, failing this, the ortho-position relatively to the  $\text{NH}_2$ -group. It seems reasonable to refer these results to the same cause, so that if toluidine sulphate, when baked or when heated with ordinary sulphuric acid, is converted first into the sulphamic acid, and then by intramolecular change into the sulphonic acid, similar views may be employed to represent the reactions occurring during the sulphonation of the toluidinesulphonic acids.

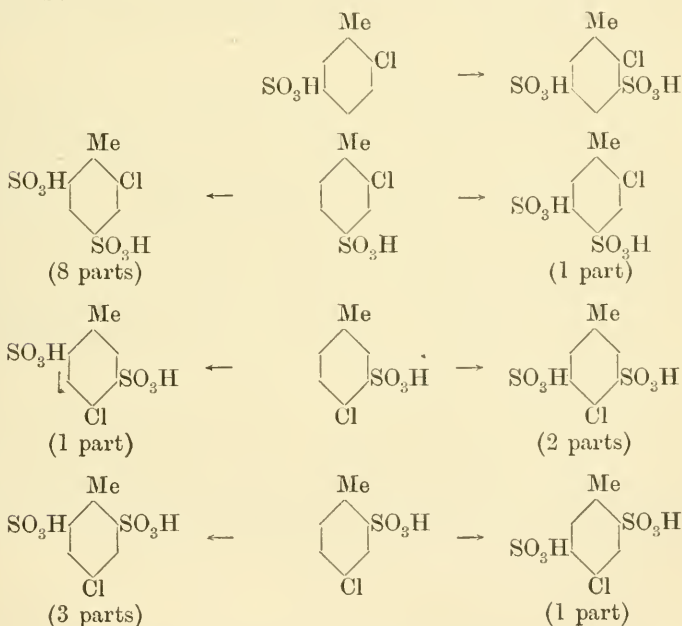


In the case of Claus and Immel's acid, sulphonation, as already stated, is effected in the cold and with anhydrosulphuric acid. These are conditions which would seem likely to favour stability of the

sulphate, and it is possible that one of the suggestions made by Miss Clare de Brereton Evans to explain the behaviour of monethylanilino under corresponding conditions (Researches on Benzenoid Amines. Thesis for the D.Sc. degree, London University, 1897, 9; Proc., 1895, 11, 235; 1896, 12, 234) may apply here, and that the sulphate becomes sulphonated at the low temperature, instead of undergoing intramolecular change.



An interesting comparison may be drawn between the behaviour of toluidine- and chlorotoluene-sulphonic acids on sulphonation. The four chlorotoluenesulphonic acids examined gave rise to the following products:



It will be seen, that whereas only one disulphonic acid is formed from each of the toluidinesulphonic acids, two are obtained from each of three out of the four chlorotoluenesulphonic acids. The disulphonic acids of corresponding constitution in the two series have their formulæ placed on the right-hand side. The list may be regarded as illustrating the result of the absence of the "directing influence" of



the  $\text{NH}_2$ -radicle, and so far as any general conclusion can be drawn, it would seem that of the three radicles present, the  $\text{SO}_3\text{H}$ -group exerts the greatest orientating effect, as the chief product in each case is that chlorotoluenedisulphonic acid which contains the  $\text{SO}_3\text{H}$ -groups in meta-positions relatively to one another.

Incidentally, the list of toluenedisulphonic acids given by Klason in his paper, "Ueber die sechs isomeren Toluoldisulfosaüre" (*loc. cit.*), has been revised. Two of the acids in this list were prepared synthetically by Klason himself; the remainder were included on the evidence for their existence adduced by their discoverers. Our experiments confirm those of Klason on the 1:2:5- and 1:3:4-derivatives, of Kornatzki on the 1:2:6-derivative (*Annalen*, 1883, 221, 200), and of Håkansson on the 1:2:4-derivative, but prove that Richter's 1:2:3-derivative (*loc. cit.*, compare Klason, *Ber.*, 1886, 19, 2889) is the 1:3:5-compound, and that the 1:3:5-acid, as described by Hasse (*loc. cit.*), does not exist. At the present time, therefore, five of the six theoretically possible toluenedisulphonic acids are known, and experiments are in progress with the object of obtaining the missing 1:2:3-isomeride.

The method for the preparation of mercaptans (or disulphides) by hydrolysis of the xanthates by alcoholic potash, gave rise to an unexpectedly large proportion of thio-ether in three of the four reactions examined, so that on oxidation with permanganate much sulphone-sulphonic acid was obtained mixed with the disulphonic acid. This is probably due to a tendency, in the case of these toluene derivatives, for the xanthate to undergo hydrolysis with alkali, not only in the manner indicated by Leuckart (*loc. cit.*, 187), but also to lose  $\text{COS}$  and yield the thio-ether,  $\text{OEt}\cdot\text{CS}\cdot\text{S}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{SO}_3\text{H} = \text{COS} + \text{EtS}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{SO}_3\text{H}$ ; a reaction hitherto observed only when xanthates have been decomposed by heat (*loc. cit.*, 184).

The authors' thanks are due to Mr. W. J. Pope for kindly furnishing the many crystallographic notes and reports included in this paper; to Mr. A. Greeves for preparing much of the isomeric toluidine-monosulphonic acids used in the investigation, and to Mr. S. Young for the determinations of nitrogen in the various anilides.

## I. TOLUIDINEDISULPHONIC ACIDS.

### *Paratoluidine-3:5-disulphonic Acid.*

The paratoluidine-3-sulphonic acid (Nevile and Winther's acid) required for the preparation of this disulphonic acid was obtained by adding the requisite quantity of concentrated sulphuric acid to paratoluidine, and heating the acid sulphate in an open dish until the

mass became dry and all reaction ceased. No evidence of the occurrence of the isomeric acid in the product could be found during the course of purification.

The monosulphonic acid was sulphonated by Richter (*Annalen*, 1885, 230, 314) by means of chlorosulphonic acid or fuming sulphuric acid. We employed the former agent, following Richter's directions, and, after verifying his statements as to the uniformity of the product and the composition of the barium and potassium salts, proceeded to convert it on the one hand into toluenedisulphonic acid, and on the other into chlorotoluenedisulphonic acid.

The toluenedisulphonic acid was obtained by Richter by reducing the corresponding potassium iodotoluenedisulphonate in aqueous solution with sodium amalgam. We obtained the same acid by employing von Baeyer's hydrazine method for the elimination of the  $\text{NH}_2$ -radicle of the toluidinedisulphonic acid. For this purpose, the potassium salt was dissolved in the smallest possible quantity of water, precipitated with hydrochloric acid, diazotised, and reduced with the requisite quantity of a solution of stannous chloride in hydrochloric acid. The hydrazine derivative separated in very soluble, small, pale yellow scales, and, after filtration and careful washing with small quantities of water to remove hydrochloric acid as far as possible, was oxidised with copper sulphate solution, giving a good separation of cuprous oxide. After removal of the excess of copper by precipitation with hydrogen sulphide, the filtrate was freed from excess of sulphuric acid by means of baryta, and the barium and potassium salts prepared. The former, with  $3\frac{1}{2}\text{H}_2\text{O}$ , agreed with Richter's description, the latter crystallised in very soluble, small, thin scales, which, after exposure to the air for a short time, were found to be anhydrous, and not monhydrated as stated. The chloride was easily soluble in benzene, and crystallised from a mixture of benzene and light petroleum in small prisms which melted at  $95^\circ$ , and thus agreed with Richter's description. A comparison of this toluenedisulphonic chloride with that from orthotoluidine-3:5-disulphonic acid was made by Mr. W. J. Pope, who found them to be crystallographically identical. The anilide melted at  $153^\circ$ , and on fusion with an equal quantity of the toluene-3:5-disulphonic anilide prepared from orthotoluidine-3:5-disulphonic acid, formed a mixture which, after solidification, again melted at  $153^\circ$ . It follows, therefore, that Richter's toluenedisulphonic acid is the 1:3:5- and not the 1:2:6- or 1:2:3-derivative, as he was led to think.

*Parachlorotoluene-3:5-disulphonic acid* was prepared by stirring diazotised paratoluidine-3:5-disulphonic acid into a lukewarm solution of cuprous chloride in hydrochloric acid. The copper salt of the chloro-acid separated during the addition of the diazo-com-

pound, but dissolved on warming the solution, and crystallised on cooling in small green scales. After removal of the copper by hydrogen sulphide, the acid was obtained from the concentrated solution in very soluble, long, colourless needles.

The *barium* salt,  $C_6H_2MeCl(SO_3)_2Ba + 3H_2O$ , obtained either directly, or by hydrolysing the chloride with baryta, crystallised from water in small, well-defined, fairly soluble prisms.

0.2694 lost 0.031  $H_2O$  at  $210^\circ$ .  $H_2O = 11.51$ , theory = 11.35.

0.2384 dry salt gave 0.1292  $BaSO_4$ .  $Ba = 31.87$ , theory = 32.50.

The *potassium* salt,  $C_6H_2MeCl(SO_3K)_2 + 6H_2O$ , crystallised from water in long, thin, easily soluble needles, which rapidly effloresced on exposure to the air, becoming opaque and anhydrous.

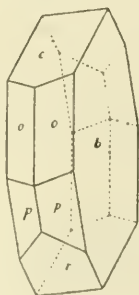
0.4835 lost 0.1101  $H_2O$  at  $205^\circ$ .  $H_2O = 22.77$ ; theory = 22.95.

0.3734 dry salt gave 0.1788  $K_2SO_4$ .  $K = 21.46$ , theory = 21.52.

The *chloride*,  $C_6H_2MeCl(SO_2Cl)_2$ , crystallised from benzene, in which it was easily soluble, in small, elongated prisms, hopper like crystals also separating on the surface of the solvent as a rule. These crystals contained  $\frac{1}{2}$  mol. prop. of benzene, which is only partially lost during prolonged exposure to the air, but is completely and rapidly expelled on heating at  $140^\circ$ . They softened at  $78-80^\circ$ , melted at  $80-100^\circ$ , and, after heating to expel the benzene, fused constantly at  $118^\circ$ . Mr. W. J. Pope examined these crystals, and reported as follows.

"The crystals which contain  $\frac{1}{2}C_6H_6$  are small, very brilliant, colourless prisms, belonging to the monosymmetric system (Fig. 1); they are iridescent and opalescent, and possess a calcite-like lustre. The dominant form is  $b\{010\}$ , but the pinacoid  $c\{001\}$  is frequently very large; the forms  $o\{111\}$  and  $p\{110\}$  are of about equal size, and  $r\{\bar{1}01\}$  is usually well developed. The reflections obtained from all these forms are, in general, poor in character. Traces of the form  $r'\{101\}$  are occasionally observed. Owing to the opacity of the crystals, no optical examination was possible.

FIG. 1.



"Crystalline System.—Monosymmetric.

$$a : b : c = 0.7043 : 1 : 1.0262.$$

$$\beta = 74^\circ 11.5'.$$

"Forms observed.— $b\{010\}$ ,  $c\{001\}$ ,  $p\{110\}$ ,  $r\{\bar{1}01\}$ ,  $r'\{101\}$ , and  $o\{111\}$ .

"The following angular measurements were obtained.

Angle.	Number of observations.	Limits.	Mean.	Calculated.
$bp = 010 : 110$	15	$55^\circ 45' - 56^\circ 1'$	$55^\circ 53'$	$55^\circ 52.5'$
$pp = 110 : \bar{1}\bar{1}0$	12	$68 \ 6 - 68 \ 24$	$68 \ 13$	$68 \ 15$
$bo = 010 : 111$	37	$63 \ 19 - 63 \ 38$	$63 \ 29$	—
$oo = 111 : \bar{1}\bar{1}\bar{1}$	19	$52 \ 54 - 53 \ 9$	$52 \ 59$	$53 \ 2$
$co = 001 : 111$	28	$50 \ 43 - 51 \ 14$	$50 \ 50$	—
$op = 111 : 110$	32	$25 \ 50 - 26 \ 39$	$26 \ 8$	—
$cp = 001 : 110$	14	$76 \ 37 - 77 \ 18$	$76 \ 56$	$76 \ 58$
$cr = 00\bar{1} : 110$	34	$102 \ 33 - 103 \ 39$	$103 \ 2$	$103 \ 2$
$pr = \bar{1}10 : \bar{1}01$	7	$49 \ 51 - 50 \ 24$	$50 \ 4$	$50 \ 1$
$pr' = 110 : \bar{1}01$	8	$129 \ 37 - 130 \ 6$	$129 \ 51$	$129 \ 59$
$cr' = 001 : 101$	4	$65 \ 49 - 67 \ 26$	$66 \ 31$	$66 \ 44''$

The chloride dissolved readily in ether and ethylic acetate, sparingly in light petroleum (b. p.  $45-90^\circ$ ), and crystallised from these solvents in small plates melting at  $118^\circ$ . These crystals were examined by Mr. W. J. Pope, who reported as follows.

"The compound melting at  $118^\circ$  is fairly soluble in ethylic acetate, and the cold solution on spontaneous evaporation deposits colourless, tabular, tetragonal crystals (Fig. 2), which contain no solvent of crystallisation. The crystals can readily be obtained of 1 cm. in diameter; they possess a glassy lustre, are very brilliant and transparent, and show an internal hour-glass shaped structure when rapidly deposited.

"The dominant form is always  $c\{001\}$ , and the dome form  $q\{101\}$  is usually well developed. The pyramids  $o\{111\}$  and  $o'\{11\bar{3}\}$  are made up of long, narrow faces, which are, however, larger than those of the prism  $p\{110\}$ ; the latter form is frequently absent. All the forms give good results on measurement with the exception of the pinacoid  $c\{001\}$ , the faces of which are usually striated in accordance with the internal structure.

FIG. 2.



"*Crystalline System.*—Tetragonal.

$$a : c = 1 : 1.3647.$$

"*Forms observed.*— $c\{001\}$ ,  $p\{110\}$ ,  $q\{101\}$ ,  $o\{111\}$ , and  $o'\{113\}$ .

"If  $o\{111\}$  be made  $\{101\}$  then

$$a : c = 1 : 1.9299,$$

and if  $o'\{113\}$  be made  $\{101\}$  then

$$a : c = 1 : 0.6433.$$

"The following angular measurements were obtained.

Angle.	Number of observations.	Limits.	Mean.	Calculated.
$cq = 001 : 101$	47	$53^{\circ}21' - 54^{\circ}8'$	$53^{\circ}46'$	—
$qq = 101 : 10\bar{1}$	45	$72^{\circ}3' - 72^{\circ}48'$	$72^{\circ}29'$	$72^{\circ}28'$
$co = 001 : 111$	12	$62^{\circ}18' - 62^{\circ}50'$	$62^{\circ}31'$	$62^{\circ}36.5'$
$co' = 001 : 11\bar{3}$	16	$32^{\circ}16' - 33^{\circ}0'$	$32^{\circ}40'$	$32^{\circ}45'$
$oo' = 111 : 11\bar{3}$	28	$29^{\circ}31' - 30^{\circ}7'$	$29^{\circ}52'$	$29^{\circ}51'$
$op = 111 : 110$	6	$27^{\circ}2' - 27^{\circ}54'$	$27^{\circ}25'$	$27^{\circ}23.5'$
$oo = 111 : 11\bar{1}$	11	$54^{\circ}38' - 55^{\circ}14'$	$54^{\circ}53'$	$54^{\circ}47'$
$pq = 110 : 101$	8	$54^{\circ}47' - 55^{\circ}36'$	$55^{\circ}9'$	$55^{\circ}13.5'$
$qq = 101 : 011$	4	$69^{\circ}25' - 70^{\circ}1'$	$69^{\circ}41'$	$69^{\circ}33'$
$qo = 101 : 111$	9	$38^{\circ}26' - 39^{\circ}7'$	$38^{\circ}44'$	$38^{\circ}53'$
$oo = 111 : 11\bar{1}$	5	$101^{\circ}59' - 102^{\circ}46'$	$102^{\circ}28'$	$102^{\circ}13'$

"The characteristic interference figure of a uniaxial material may be observed by microscopic examination through the form  $c\{001\}$ ; the double refraction is positive in sign and very weak.

"It is interesting to note that crystals having the same geometrical constants and appearance are sometimes deposited on spontaneous evaporation of a solution in a mixture of benzene and petroleum; these crystals contain no benzene of crystallisation, and measurement showed that they exhibit the same angles and the same forms as those from ethylic acetate solution to which the above description refers. The crystals of which mention is now made, however, are sometimes optically anomalous, in that they are frequently biaxial; the optic axial angle is variable in size, but often quite large, being usually largest in the middle of the face  $c(001)$ . The optic axial plane seems always parallel to the plane  $a(100)$ ."

From mixtures of benzene with light petroleum, the chloride usually crystallised with benzene in the first form, but from mixtures of benzene with petroleum (b. p.  $90-120^{\circ}$ ), usually in the second form.

2.82 lost 0.0816 benzene after exposure in a current of air during



6 days, and an additional 0.2144 benzene after heating at  $140^{\circ}$  during an hour.\*  $C_6H_6 = 10.50$ , theory = 10.77.

0.1192 chloride, m. p. =  $118^{\circ}$ , gave 0.1586 AgCl. Cl = 32.91; theory = 32.92.

The *anilide*,  $C_6H_2MeCl(SO_2NHPh)_2$ , crystallised from either benzene or alcohol in radiate groups of elongated scales, sparingly soluble in benzene, readily in alcohol or ether; it melted at  $184^{\circ}$ .

0.5626 gave 29 c.c. moist nitrogen at  $15.5^{\circ}$  and 756 mm. N = 6.06, theory = 6.41.

*Paratoluidine-2:5-disulphonic Acid.*

The paratoluidine-2-sulphonic acid required for the preparation of this disulphonic acid was prepared from purified potassium paranitrotoluene-2-sulphonate by reduction with iron and sulphuric acid and conversion into the potassium paratoluidinesulphonate, which was twice crystallised, and subsequently precipitated by hydrochloric acid in the usual way.

The monosulphonic acid was sulphonated by Richter (*loc. cit.*, 331) by means of chlorosulphonic acid or fuming sulphuric acid; in our experiments, the former was employed, and, contrary to Richter's experience, reaction set in at once in the cold, being completed at  $150^{\circ}$  as he describes. After verifying his statements as to the composition of the barium and potassium salts, and ascertaining that the product was uniform, the crystallised potassium salt was converted on the one hand into toluenedisulphonic acid, and, on the other, into chlorotoluenedisulphonic acid.

The toluenedisulphonic acid from this source has not been described. We obtained it by the hydrazine method; the hydrazine derivative crystallised in small, pale buff scales, was easily freed from acid by washing with small quantities of water, and gave a considerable separation of cuprous oxide on oxidation with copper sulphate solution. The barium and potassium salts, both with  $1H_2O$ , were identical with those of toluene-2:5-disulphonic acid. The chloride crystallised from benzene, or from a mixture of benzene and light petroleum in prisms, melted at  $98^{\circ}$ , and, on fusion with an equal amount of the chloride prepared from orthotoluidine-5-sulphonic acid by the xanthate method (see further), formed a mixture which, after solidification, melted at  $98^{\circ}$ . The identity of the two was also established by crystallographic examination. The anilide melted at

\* At this temperature, a constant loss of 0.0047 gram per hour was observed and attributed to volatilisation of the chloride, as the melting point of the residue was not affected after heating during 6 hours. The necessary correction was applied in calculating the loss of benzene after heating during a known period.

178°, and its melting point was not affected by mixture with toluene-2:5-disulphonic anilide. It follows, therefore, that the toluenedisulphonic acid corresponding with Richter's second paratoluidine-disulphonic acid is the 1:2:5-derivative.

*Parachlorotoluene-2:5-disulphonic acid* was prepared by stirring diazotised paratoluidine-2:5-disulphonic acid into a lukewarm solution of cuprous chloride in hydrochloric acid. It crystallised from the concentrated acid solution, after removal of the copper, in very soluble small scales.

The *barium* salt,  $C_6H_2MeCl(SO_3)_2Ba + H_2O$ , obtained by hydrolysing the chloride with baryta, crystallised from water in sparingly soluble, minute prisms.

0.462 lost 0.0194  $H_2O$  at 235°.  $H_2O = 4.20$ , theory = 4.10.

0.4426 dry salt gave 0.2446  $BaSO_4$ .  $Ba = 32.49$ , theory = 32.50.

The *potassium* salt,  $C_6H_2MeCl(SO_3K)_2 + 2H_2O$ , crystallised from water in easily soluble, small, glistening scales.

0.191 lost 0.017  $H_2O$  at 180°.  $H_2O = 8.90$ , theory = 9.04.

0.174 dry salt gave 0.0838  $K_2SO_4$ .  $K = 21.58$ , theory = 21.52.

The *chloride*,  $C_6H_2MeCl(SO_2Cl)_2$ , crystallised from benzene in very small prisms, melted at 144°, and was not very soluble in benzene, and almost insoluble in ether and in light petroleum.

0.1323 gave 0.1773  $AgCl$ .  $Cl = 33.14$ , theory = 32.92.

Mr. W. J. Pope examined the crystals and reported as follows.

"The crystals consist of small colourless and transparent rectangular scales, showing straight extinction; the large face is perpendicular to a bisectrix. After melting, the material solidifies very readily, giving a film consisting of long, individual crystalline flakes, many of which are perpendicular to the negative bisectrix of a large optic axial angle. The film is full of air-holes and cracks."

The *anilide*,  $C_6H_2MeCl(SO_2NHPh)_2$ , crystallised from alcohol in small, diamond-shaped scales, from acetone in large, well-developed prisms, and melted at 245°. It was very sparingly soluble in benzene, sparingly in alcohol, and easily in acetone.

0.7359 gave 39.7 c.c. moist nitrogen at 14.5° and 771 mm.

$N = 6.52$ , theory = 6.41.

#### *Orthotoluidine-4:5-disulphonic Acid.*

Orthotoluidine-4-sulphonic acid was prepared by Claus and Immel (*Annalen*, 1891, 265, 71) by sulphonating crystallised orthotoluidine sulphate with twice its weight of 50 per cent. anhydrosulphuric acid

at temperatures below  $0^{\circ}$ . Equally good results, we found, were obtained by using twice the weight of 30 per cent. anhydrosulphuric acid. The acid was placed in a flask, and cooled below  $0^{\circ}$  in a freezing mixture, becoming semi-solid, but soon liquefying after some of the orthotoluidine sulphate was dusted in. During the addition of the sulphate, the temperature was kept below  $3^{\circ}$ , and when completed the mixture was left in an ice bath all night, allowed to remain at the temperature of the laboratory during an hour on the following day, and afterwards poured on to crushed ice. The product was converted into barium salt in the usual way; during neutralisation the odour of sulphurous anhydride was very noticeable, and some orthotoluidine was invariably recovered. The yield of sulphonic acid rarely exceeded 80 per cent. of that theoretically possible from the quantity of orthotoluidine sulphate employed. The barium salt, with  $2\frac{1}{2}\text{H}_2\text{O}$ , and calcium salt, with  $6\text{H}_2\text{O}$ , agreed with the descriptions given by Hayduck (*ibid.*, 1874, 172, 205) and by Claus and Immel.

The *potassium* salt,  $\text{NH}_2\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{SO}_3\text{K} + \text{H}_2\text{O}$ , crystallised from water in very soluble, small, lustrous scales.

0.4702 lost 0.0348  $\text{H}_2\text{O}$  at  $180^{\circ}$ .  $\text{H}_2\text{O} = 7.40$ , theory = 7.41.

0.4354 dry salt gave 0.1672  $\text{K}_2\text{SO}_4$ .  $\text{K} = 17.21$ , theory = 17.33.

An examination was made to ascertain whether Nevile and Winther's orthotoluidine-5-sulphonic acid was formed under the conditions employed, but no evidence could be obtained of its presence.

*Orthotoluidine-4:5-disulphonic acid* was obtained by sulphonating orthotoluidine-4-sulphonic acid (100 grams) with chlorosulphonic acid (75 grams) under conditions similar to those employed by Richter and by Hasse in the case of isomeric acids. Evolution of hydrogen chloride commenced at about  $110^{\circ}$ ; the mass became pasty at about  $130^{\circ}$ ; it was then heated at  $150^{\circ}$  during 2 hours and at  $160^{\circ}$  during a third hour. The hard, dry, brown mass was mixed with water, evaporated over steam to remove hydrogen chloride as far as possible, and finally dissolved in water. The solution gave a considerable amount of a sparingly soluble substance in minute needles, which proved to be the expected disulphonic acid, whilst the mother liquors, on examination, were found to contain nothing but orthotoluidine-4-sulphonic acid, which was recognised both by the great solubility of its salts and by conversion into the corresponding chlorotoluene-4-sulphonic chloride melting at  $37^{\circ}$ . The disulphonic acid seemed to be uniform, and no evidence could be obtained of the presence of an isomeride.

The *barium* salt,  $\text{NH}_2\cdot\text{C}_6\text{H}_2\text{Me}(\text{SO}_3)_2\text{Ba} + 1\frac{1}{2}\text{H}_2\text{O}$ , crystallised from water in sparingly soluble, small, thin scales, and when separated

from a hot solution during concentration was much less soluble than the crystallised form, owing possibly to dehydration.

0.3514 lost 0.0218  $\text{H}_2\text{O}$  at  $200^\circ$ .  $\text{H}_2\text{O} = 6.20$ , theory = 6.29.

0.3296 dry salt gave 0.1868  $\text{BaSO}_4$ .  $\text{Ba} = 33.32$ , theory = 34.08.

The *potassium* salt,  $\text{NH}_2\cdot\text{C}_6\text{H}_2\text{Me}(\text{SO}_3\text{K})_2 + 2\text{H}_2\text{O}$ , crystallised from water in easily soluble, thin scales, or, occasionally, from more concentrated solutions in anhydrous, short, slender needles.

0.2033, scales, lost 0.0207  $\text{H}_2\text{O}$  at  $200^\circ$ .  $\text{H}_2\text{O} = 10.18$ , theory = 9.50.

0.1826 dry salt gave 0.0926  $\text{K}_2\text{SO}_4$ .  $\text{K} = 22.73$ , theory = 22.74.

The orientation of the sulphonic radicles in this acid was ascertained by eliminating the  $\text{NH}_2$ -group by the hydrazine method. The crystallised potassium salt was employed, and as the precipitate formed by adding hydrochloric acid to its concentrated aqueous solution was found to take up nitrite very slowly, it was finely ground in a mortar to obviate this difficulty. The diazo-compound consisted of sparingly soluble, colourless, microscopic needles, and the hydrazine derivative of sparingly soluble, small, slender needles. After careful washing with small quantities of water, the hydrazine gave a good reaction with copper sulphate solution. The barium salt, with  $2\text{H}_2\text{O}$ , and potassium salt, with  $1\text{H}_2\text{O}$ , of the toluenedisulphonic acid thus obtained resembled both in solubility and appearance the corresponding salts of the 1 : 3 : 4-derivative prepared from Neville and Winther's paratoluidine-3-sulphonic acid by Klason, and by the xanthate method to be described presently. The chloride crystallised both with benzene of crystallisation in prisms which became opaque on exposure to air, and without benzene in plates melting at  $111^\circ$ . The anilide melted at  $190^\circ$ , and when fused with an equal quantity of toluene-3 : 4-disulphonic anilide, formed a mixture which, after solidification, again melted at  $190^\circ$ .

*Orthochlorotoluene-4 : 5-disulphonic acid* was prepared from potassium orthotoluidine-4 : 5-disulphonate by Sandmeyer's method in the usual way. During the reaction between the diazo-compound and the acid cuprous chloride solution, a considerable quantity of the *hydrogen potassium* salt,  $\text{SO}_3\text{H}\cdot\text{C}_6\text{H}_2\text{MeCl}\cdot\text{SO}_3\text{K} + \text{H}_2\text{O}$ , separated as a micro-crystalline powder which dissolved on heating the solution, but crystallised again on cooling. It was also sparingly soluble in water.

0.1607 lost 0.009  $\text{H}_2\text{O}$  at  $180^\circ$ .  $\text{H}_2\text{O} = 5.60$ , theory = 5.25.

0.1517 dry salt gave 0.0411  $\text{K}_2\text{SO}_4$ .  $\text{K} = 12.14$ , theory = 12.02.

The *barium* salt,  $\text{C}_6\text{H}_2\text{MeCl}(\text{SO}_3)_2\text{Ba} + 2\text{H}_2\text{O}$ , prepared by hydrolysing the chloride with baryta, crystallised from water in very sparingly soluble, small, rectangular prisms.



0.413 lost 0.032  $\text{H}_2\text{O}$  at  $250^\circ$ .  $\text{H}_2\text{O} = 7.75$ , theory = 7.87.

0.381 dry salt gave 0.209  $\text{BaSO}_4$ .  $\text{Ba} = 32.23$ , theory = 32.50.

The *potassium* salt,  $\text{C}_6\text{H}_2\text{MeCl}(\text{SO}_3\text{K})_2 + \text{H}_2\text{O}$ , crystallised from water in easily soluble, long, prismatic needles.

0.4168 gave 0.0204  $\text{H}_2\text{O}$  at  $180^\circ$ .  $\text{H}_2\text{O} = 4.89$ , theory = 4.73.

0.3964 dry salt gave 0.1898  $\text{K}_2\text{SO}_4$ .  $\text{K} = 21.46$ , theory = 21.52.

The *chloride*,  $\text{C}_6\text{H}_2\text{MeCl}(\text{SO}_2\text{Cl})_2$ , which crystallised from benzene in lustrous, small, well-developed prisms, dissolved somewhat sparingly in benzene, was almost insoluble in ether and in light petroleum, and melted at  $158^\circ$ . Mr. W. J. Pope made the following report on the crystals.

"This substance crystallises by spontaneous evaporation of its chloroform solution in very lustrous, transparent plates or prisms belonging to the monosymmetric system; although the habit of the crystals is very variable, the largest face is usually perpendicular to the acute bisectrix. The optic axial angle is small, and the double refraction is positive in sign and very weak."

0.1054 gave 0.1399  $\text{AgCl}$ .  $\text{Cl} = 32.84$ , theory = 32.92.

The *anilide*,  $\text{C}_6\text{H}_2\text{MeCl}(\text{SO}_2\text{NHPh})_2$ , crystallised in small prisms either from alcohol or from a mixture of benzene and light petroleum, dissolved easily in benzene but only sparingly in alcohol, and melted at  $183^\circ$ .

0.6866 gave 36.4 c.c. moist nitrogen at  $16^\circ$  and 764 mm.

$\text{N} = 6.31$ , theory = 6.41.

#### *Orthotoluidine-3:5-disulphonic Acid.*

Orthotoluidine-3:5-disulphonic acid was prepared by Nevile and Winther from their orthotoluidine-5-sulphonic acid by heating it with fuming sulphuric acid (Trans., 1882, 41, 421), and, although neither the acid nor its salts were described, the constitution was established by conversion of the disulphonic acid into 3:5-dinitro-orthocresol. Hasse obtained the same acid by sulphonating the monosulphonic acid either with chlorosulphonic acid or fuming sulphuric acid, and described the salts and a number of derivatives (*Annalen*, 1885, 230, 286). We employed chlorosulphonic acid as the sulphonating agent, and, after confirming Hasse's statements with reference to the salts, converted the toluidinedisulphonic acid into the corresponding toluene-disulphonic acid on the one hand, and into the chloro- and bromo-toluenedisulphonic acids on the other.

A toluenedisulphonic acid was prepared by Nevile and Winther



from this source by boiling the diazo-compound with alcohol (*loc. cit.*), but neither the acid nor its salts were described. Hasse states that he obtained the acid by reducing either the corresponding bromotoluene-disulphonic acid with sodium amalgam, or the iodo-acid with concentrated hydriodic acid. The former method gave a product which was evidently impure, whilst the latter, from the conditions employed, could not be expected to lead to a satisfactory result. As obtained by the hydrazine method, the acid differs in its properties from that described by Hasse, as will be seen from a description of its salts and chloride. The hydrazine derivative obtained from the ortho-toluidinedisulphonic acid was a pale yellow, easily soluble, micro-crystalline compound, which, after careful washing with small quantities of water, gave a good separation of cuprous oxide on oxidation with copper sulphate solution.

*Barium toluene-3:5-disulphonate*,  $C_6H_3Me(SO_3)_2Ba + 3\frac{1}{2}H_2O$ , crystallised from water in easily soluble, small prisms.

0.1878 lost 0.026  $H_2O$  at  $210^\circ$ .  $H_2O = 13.84$ , theory = 14.00.

0.1618 dry salt gave 0.0958  $BaSO_4$ .  $Ba = 34.81$ , theory = 35.40.

The *potassium* salt,  $C_6H_3Me(SO_3K)_2$ , crystallised from water or from dilute alcohol in very soluble, microscopic scales which were anhydrous. Hasse found  $2\frac{1}{2}H_2O$ .

0.1927 lost 0.0012  $H_2O$  at  $200^\circ$ , and gave 0.1019  $K_2SO_4$ .

$K = 23.58$ , theory = 23.78.

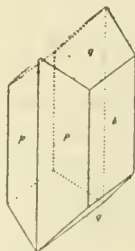
The *chloride*,  $C_6H_3Me(SO_2Cl)_2$ , crystallised from a mixture of benzene and light petroleum in pale yellow, prismatic forms, which melted at  $95^\circ$ , and not at  $132^\circ$  as Hasse states.

0.2407 gave 0.2383  $AgCl$ .  $Cl = 24.49$  (Hasse 25.9), theory = 24.57.

Mr. W. J. Pope has examined the crystals and reports as follows.

"The crystals consist of small, poorly developed, and almost opaque yellowish prisms belonging to the monosymmetric system (Fig. 3). The form  $b\{010\}$  is usually dominant, and the prism  $p\{110\}$  is also large; the form  $q\{011\}$  is usually small. None of the faces give good results on measurement.

FIG. 3.



*Crystalline System.*—Monosymmetric.

$$a : b : c = 0.8132 : 1 : 0.8990.$$

$$\beta = 82^\circ 5'$$

*Forms observed.*— $b\{010\}$ ,  $p\{110\}$ , and  $q\{011\}$ .

“The following angular measurements were obtained.

Angle.	Number of observations.	Limits.	Mean.	Calculated.
$bp = 010 : 110$	32	$50^\circ 4' - 52^\circ 9'$	$51^\circ 11'$	$51^\circ 9'$
$pp = 110 : \bar{1}10$	26	$101^\circ 24' - 103^\circ 17'$	$102^\circ 18'$	$102^\circ 18'$
$pp = 110 : \bar{1}\bar{1}0$	36	$77^\circ 3' - 78^\circ 54'$	$77^\circ 42'$	—
$bq = 010 : 011$	14	$47^\circ 30' - 49^\circ 11'$	$48^\circ 17'$	$48^\circ 19'$
$qq = 011 : 01\bar{1}$	29	$95^\circ 48' - 97^\circ 45'$	$96^\circ 36'$	$96^\circ 38'$
$qq = 011 : 0\bar{1}1$	37	$82^\circ 51' - 84^\circ 2'$	$83^\circ 22'$	—
$pq = 110 : 01\bar{1}$	21	$69^\circ 33' - 71^\circ 8'$	$70^\circ 17'$	—
$pq = 110 : 0\bar{1}1$	10	$108^\circ 54' - 110^\circ 6'$	$109^\circ 36'$	$109^\circ 43'$

“After melting, the substance solidifies readily from centres in long needles, showing an extinction straight from the centre of crystallisation. The needles on microscopic examination sometimes show an optic axis, but usually the acute bisectrix of a fairly large optic axial angle emerges in the field; the double refraction is positive in sign. The film is now very transparent, but after a short time one or other of the circles of growth in the film becomes bordered with another crystalline modification which appears much more opaque than the first. The film ultimately shows aggregate polarisation, but retains the trace of the first structure.”

The *anilide*,  $C_6H_5Me(SO_2NHPh)_2$ , crystallised either from benzene or dilute alcohol in thin scales, dissolved sparingly in benzene, readily in alcohol or ether, and melted at  $153^\circ$ .

0.381 gave 23.1 c.c. moist nitrogen at  $21^\circ$  and 763 mm.

$$N = 7.1, \text{ theory} = 6.96.$$

*Orthobromotoluene-3:5-disulphonic acid.*—This acid was described by Hasse and utilised for the preparation of the toluenedisulphonic acid. In view of the discrepancy between his results and ours, it seemed possible that his bromo-acid might have been impure, and a repetition of the work supports this view. The bromo-acid was prepared from orthotoluidine-3:5-disulphonic acid by Sandmeyer's method.

The *barium* salt,  $C_6H_2MeBr(SO_3)_2Ba + 4H_2O$ , prepared from the chloride by hydrolysis with baryta, crystallised in very short, slender needles. Hasse found  $1\frac{1}{2}H_2O$ .

0.1951 lost  $0.026 H_2O$  at  $210^\circ$ .  $H_2O = 13.33$ , theory = 13.38.

0.1691 dry salt gave  $0.0845 BaSO_4$ .  $Ba = 29.38$ , theory = 29.40.

The *potassium* salt,  $C_6H_2MeBr(SO_3K)_2 + H_2O$ , crystallised from water in clusters of very soluble, small needles. Hasse described the salt as crystallising in tabular forms with  $4H_2O$ .

0.1889 lost 0.0086  $H_2O$  at  $200^\circ$ .  $H_2O = 4.55$ , theory = 4.23.

0.1803 dry salt gave 0.078  $K_2SO_4$ .  $K = 19.39$ , theory = 19.16.

The *chloride*,  $C_6H_2MeBr(SO_2Cl)_2$ , crystallised either from benzene or from a mixture of benzene and light petroleum in small, white aggregates of needles, dissolved readily in benzene and ether, sparingly in light petroleum, and melted at  $102^\circ$ . Hasse's product crystallised in prisms melting at  $90^\circ$ .

0.2146 gave 0.2787 of mixed  $AgCl$  and  $AgBr$ .

$Cl = 19.40$ , theory 19.29 ;  $Br = 21.89$ , theory = 21.74.

The *anilide*,  $C_6H_2MeBr(SO_2NHPh)_2$ , which crystallised from benzene in very small, square prisms, and from dilute alcohol in short, irregular needles, dissolved sparingly in benzene, easily in alcohol, and melted at  $194^\circ$ .

0.3688 gave 17.45 c.c. moist nitrogen at  $16^\circ$  and 764 mm.

$N = 5.63$ , theory = 5.82.

*Orthochlorotoluene-3 : 5-disulphonic acid*, prepared by stirring diazotised orthotoluidinedisulphonic acid into a lukewarm solution of cuprous chloride in hydrochloric acid, crystallised from concentrated solutions in very small and very soluble needles.

The *barium* salt,  $C_6H_2MeCl(SO_3)_2Ba + \frac{1}{2}H_2O$ , obtained by hydrolysis of the chloride, was very soluble in water, and crystallised in minute needles.

0.2704 lost 0.0434  $H_2O$  at  $250^\circ$ .  $H_2O = 16.05$ , theory = 16.12.

0.227 dry salt gave 0.1243  $BaSO_4$ .  $Ba = 32.19$ , theory = 32.50.

The *potassium* salt,  $C_6H_2MeCl(SO_3K)_2 + 2\frac{1}{2}H_2O$ , crystallised very slowly from water in easily soluble large, massive, irregular crystals.

0.1598 lost 0.0184  $H_2O$  at  $200^\circ$ .  $H_2O = 11.51$ , theory = 11.04.

0.1414 dry salt gave 0.0678  $K_2SO_4$ .  $K = 21.49$ , theory = 21.52.

From dilute alcohol, the salt separated in small spherical aggregates of needles with  $2H_2O$ .

0.339 lost 0.0288  $H_2O$  at  $195^\circ$ .  $H_2O = 8.50$ , theory = 9.03.

The *chloride*,  $C_6H_2MeCl(SO_2Cl)_2$ , crystallised from a mixture of benzene and light petroleum in radiate groups of short, slender needles, dissolved easily in benzene and ether, sparingly in light petroleum, and melted at  $85^\circ$ .

0.0832 gave 0.1112  $AgCl$ .  $Cl = 33.06$ , theory = 32.92.

The *anilide*,  $C_6H_2MeCl(SO_2NHPh)_2$ , crystallised from benzene, and from dilute alcohol in small, elongated, flat prisms, dissolved sparingly in benzene, easily in alcohol, and melted at  $183^\circ$ .

0.3785 gave 20.2 c.c. moist nitrogen at  $16^\circ$  and 768 mm.

N = 6.39, theory = 6.41.

## II. TOLUENEDISULPHONIC ACIDS.

*Toluene-3:4-disulphonic Acid from Paratoluidine-3-sulphonic Acid by the Xanthate Method.*

Toluene-3:4-disulphonic acid was obtained by Klason from paratoluidine-3-sulphonic acid through the intermediary of the thio-cresolsulphonic acid (*Ber.*, 1887, 20, 356). We prepared it by employing potassium xanthate in place of potassium sulphide, following Leuckart's method (*J. pr. Chem.*, 1890, [ii], 41, 218), and oxidising the resulting disulphide-sulphonate to disulphonic acid by potassium permanganate (Farbenfab. vorm. F. Bayer & Co., D.R.-P. 70296 of June 14, 1892). For this purpose, the paratoluidinesulphonic acid was diazotised in quantities of 60 grams, using as little water as possible, and the sparingly soluble, crystalline diazo-compound collected, washed, mixed with a little water, and added slowly to a concentrated solution of 35 grams of potassium xanthate. Much effervescence occurred, and the flask was cooled from time to time to prevent undue rise of temperature. A few crystalline plates separated, which on recrystallisation formed hard clusters of small, hexagonal plates, and had the composition of the *xanthate*,  $SO_3K \cdot C_6H_3Me \cdot S \cdot CS \cdot OEt + 2H_2O$ .

0.2472 lost 0.0258  $H_2O$  at  $115^\circ$ .  $H_2O = 10.39$ , theory = 9.83.

0.2214 dry salt gave 0.0598  $K_2SO_4$ .  $K = 12.16$ , theory = 11.82.

This salt decomposed into the thio-ether,  $SO_3K \cdot C_6H_3Me \cdot SEt$ , no doubt by loss of COS, when heated at temperatures above  $120^\circ$ , and the change was complete at  $190^\circ$ . Thus, the loss in weight at  $150^\circ$  was 11.68 per cent. ; at  $180^\circ$ , 17.20 per cent. ; at  $190^\circ$ , 25.19 per cent. ; and the product gave numbers corresponding with those required for the percentage of potassium in the thio-ether ( $K = 14.58$ , theory = 14.44).

The impure xanthate which separated and the mother liquor were hydrolysed separately by boiling with successive small quantities of alcoholic potash until permanently alkaline, and, after removal of the alcohol by distillation, the solutions were dissolved in water and concentrated to crystallising point. From the impure xanthate, the thio-ether was obtained in anhydrous, well-defined, square plates, but from the mother liquor nothing satisfactory could be isolated, probably on account of the great solubility of the expected disulphide. Both

products were oxidised with permanganate, and, after neutralising the filtrates with sulphuric acid, the former gave mainly the sulphone-sulphonate, which was readily separated by crystallisation from the more soluble disulphonate, whilst the latter gave the disulphonate mixed, in the earlier separations, with potassium sulphate. The yield of potassium toluenedisulphonate was 94 grams from 500 grams of the Neville and Winther acid, and the proportion of thio-ether was greater with this acid than with its isomerides; various attempts were made to modify the process, even to the extent of omitting the hydrolysis, and oxidising the crude xanthate with permanganate, but without success so far as the yield of disulphonate was concerned.

The barium and potassium toluene-3:4-disulphonates, with 2 and  $1\text{H}_2\text{O}$  respectively, agreed with Klason's description.

The chloride,  $\text{C}_6\text{H}_3\text{Me}(\text{SO}_2\text{Cl})_2$ , crystallised from a mixture of benzene and light petroleum, or from light petroleum, chloroform, or ether in scales, which melted at  $111^\circ$ . From concentrated solutions in benzene, it crystallised in forms which were usually free from benzene of crystallisation, appeared to consist of a number of plates aggregated together side by side, and melted at  $111^\circ$ . From more dilute solutions in benzene, the crystals were elongated, prismatic individuals, showing good end faces, and occasionally arranged as a cross by the approximation of an end face of each of four crystals; these contained a half molecular proportion of benzene of crystallisation, which was rapidly lost on exposure to the air, the crystals becoming white and opaque. The clear crystals containing benzene fused at  $70\text{--}80^\circ$ , and after loss of the benzene melted constantly at  $111^\circ$ .

8.068 lost 0.918 benzene. Benzene = 11.38, theory = 11.89.

The *anilide*,  $\text{C}_6\text{H}_3\text{Me}(\text{SO}_2\text{NHPh})_2$ , which crystallised from acetone in well developed plates, from alcohol in small, well defined prisms, and from benzene in clusters of minute plates, dissolved easily in acetone, benzene, and ether, sparingly in alcohol, very slightly in light petroleum, and melted at  $190^\circ$ .

0.423 gave 24.6 c.c. moist nitrogen at  $22^\circ$  and 764 mm.

N = 6.78, theory = 6.96.

The *thio-ether*,  $\text{SEt}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{SO}_3\text{K}$ , crystallised from water in well-defined, square, anhydrous plates.

0.2004 lost 0.0002 at  $180^\circ$  and gave 0.0652  $\text{K}_2\text{SO}_4$ .

K = 14.58, theory = 14.44.

On treatment with phosphorus pentachloride in the cold, the salt was converted into a brown liquid, which, on adding water, slowly solidified; this was insoluble in light petroleum, but easily soluble



in benzene forming a purple solution from which the *chloride*,  $\text{SEt} \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{SO}_2\text{Cl}$ , crystallised in lemon yellow, elongated plates melting at  $67^\circ$ .

0.15 gave 0.087 AgCl.  $\text{Cl} = 14.35$ , theory = 14.11.

On oxidation with potassium permanganate solution at  $40^\circ$ , the thio-ether was readily converted into the sulphone-sulphonate.

The *barium* salt,  $(\text{EtSO}_2 \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{SO}_3)_2\text{Ba} + 3\text{H}_2\text{O}$ , obtained from the chloride by hydrolysis, crystallised from water in moderately soluble radiate groups of long, slender, silky needles.

0.2255 lost 0.0154  $\text{H}_2\text{O}$  at  $220^\circ$ .  $\text{H}_2\text{O} = 6.83$ , theory = 7.53.

0.2101 dry salt gave 0.0751  $\text{BaSO}_4$ .  $\text{Ba} = 21.02$ , theory = 20.66.

The *potassium* salt,  $\text{EtSO}_2 \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{SO}_3\text{K} + \text{H}_2\text{O}$ , crystallised from water in thin, elongated, glistening scales. It melted at  $274$ – $275^\circ$ , decomposing at a slightly higher temperature.

0.3418 lost 0.02  $\text{H}_2\text{O}$  at  $180^\circ$ .  $\text{H}_2\text{O} = 5.85$ , theory = 5.63.

0.3218 dry salt gave 0.0916  $\text{K}_2\text{SO}_4$ .  $\text{K} = 12.79$ , theory = 12.91.

Attempts were made to hydrolyse this salt and obtain ethylparatolylsulphone, but without success, although it was heated with water at temperatures up to  $270^\circ$  and with varying strengths of dilute hydrochloric and sulphuric acids, at temperatures ranging from  $150^\circ$  to those at which it charred.

The *chloride*,  $\text{EtSO}_2 \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{SO}_2\text{Cl}$ , in the crude state was a sulphur-yellow solid which became colourless on the addition of water. It dissolved easily in benzene, and, on evaporation of the solvent, crystallised in colourless plates with oblique end faces and a waxy lustre, and melted at  $117^\circ$ .

0.1564 gave 0.0788 AgCl.  $\text{Cl} = 12.46$ , theory = 12.56.

The *anilide*,  $\text{EtSO}_2 \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{SO}_2\text{NHPh}$ , crystallised from dilute alcohol in elongated plates, dissolved easily in alcohol, sparingly in benzene, and melted at  $114^\circ$ .

0.6173 gave 23 c.c. moist nitrogen at  $21^\circ$  and 770 mm.

$\text{N} = 4.40$ , theory = 4.13.

The crystals were examined by Mr. W. J. Pope, who reported as follows.

"The crystals are small, rhomb-shaped, colourless, transparent scales of waxy lustre; they are very brittle, and the extinction in the large face is oblique. A section cut approximately perpendicular to the large face is perpendicular to the acute bisectrix of a fairly small

optic axial angle; the double refraction is positive in sign. After melting, the substance solidifies very slowly to a film showing aggregate polarisation."

*Toluene-2:4-disulphonic Acid from Paratoluidine-2-sulphonic Acid by the Xanthate Method.*

Toluene-2:4-disulphonic acid and its salts were described by Håkansson, who isolated the substance from the mixture of disulphonic acids obtained on sulphonating toluene (*Ber.*, 1872, 5, 1084). For purposes of comparison, we prepared it from paratoluidine-2-sulphonic acid by the xanthate process. The reaction between the diazotised acid and a concentrated solution of potassium xanthate was slow at 0°, but proceeded rapidly at the ordinary temperature. As usual, the product was warmed to near the boiling point, and on cooling there was a copious separation of small, crystalline aggregates, which seemed to decompose during purification by boiling with charcoal. The recrystallised substance proved to be the *disulphide*,  $(\text{S} \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{SO}_3\text{K})_2 + \text{H}_2\text{O}$ , which formed radiate groups of minute needles, and was easily soluble in water.

0.1414 lost 0.005  $\text{H}_2\text{O}$  at 150°.  $\text{H}_2\text{O} = 3.53$ , theory = 3.60.

0.1364 dry salt gave 0.0488  $\text{K}_2\text{SO}_4$ .  $\text{K} = 16.04$ , theory = 16.18.

Both the disulphide and the mother liquor were boiled with successive small quantities of alcoholic potash until permanently alkaline, and, after removal of the alcohol, oxidised by permanganate. The amount of sulphone-sulphonate obtained was very small, and occurred in the final mother liquors of the disulphonate. The potassium toluenedisulphonate agreed with Håkansson's description, and the yield was 112 grams from 400 grams of the amido-acid.

Barium toluene-2:4-disulphonate,  $\text{C}_6\text{H}_3\text{Me}(\text{SO}_3)_2\text{Ba} + \text{H}_2\text{O}$ , prepared from the chloride by hydrolysis, crystallised in small, silky needles, easily soluble in water. Håkansson obtained prisms crystallising with (?)  $2\text{H}_2\text{O}$ .

0.2756 lost 0.013  $\text{H}_2\text{O}$  at 220°.  $\text{H}_2\text{O} = 4.72$ , theory = 4.44.

0.2626 dry salt gave 0.1583  $\text{BaSO}_4$ .  $\text{Ba} = 35.41$ , theory = 35.40.

The chloride,  $\text{C}_6\text{H}_3\text{Me}(\text{SO}_2\text{Cl})_2$ , was easily soluble in benzene or ether, and crystallised best from petroleum (b. p. 90—120°); from this solvent, it separated in lustrous, elongated prisms or prismatic needles, which melted at 56°. Håkansson obtained large, four-sided prisms melting at 51—52°.

The *anilide*,  $\text{C}_6\text{H}_3\text{Me}(\text{SO}_2\text{NHPh})_2$ , which crystallised from dilute

alcohol in small prisms, and from benzene in minute tufts of needles, dissolved easily in alcohol and ether, sparingly in benzene, and melted at  $187^{\circ}$ .

0.4126 gave 25.8 c.c. moist nitrogen at  $24.5^{\circ}$  and 760 mm.

$N = 7.2$ , theory = 6.96.

Mr. W. J. Pope made the following report on the crystals.

"This substance crystallises from acetone in colourless, flattened plates which possess a glassy lustre and belong to the monosymmetric system (Fig. 4); the crystals are some 2 mm. in length and 0.5 mm. in thickness. The pinacoid  $b\{010\}$ , which is the tabular form, is predominant, and gives fairly good results on measurement; the form  $p\{110\}$  is usually well developed, and the measurements obtained from it are good. The pinacoid  $c\{001\}$  is generally large, whilst the form  $r\{\bar{1}01\}$  is always small, but brilliant. The small size of the crystals prevented sections being cut, and no interference figure could be observed through  $b\{010\}$  on microscopical examination; the extinction in  $b(010)$  makes  $23^{\circ}$  with the edge  $bc$ , and  $76^{\circ}$  with the edge  $bp$ .

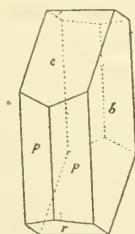
"Crystalline System.—Monosymmetric.

$a : b : c = 0.6106 : 1 : 0.5384$ .

$\beta = 53^{\circ} 31.5'$

"Forms observed.— $b\{010\}$ ,  $c\{001\}$ ,  $p\{110\}$  and  $r\{\bar{1}01\}$ .

FIG. 4.



"The following angular measurements were obtained.

Angle.	Number of observations.	Limits.	Mean.	Calculated.
$bp = 010 : 110$	42	$63^{\circ} 2' - 64^{\circ} 47'$	$63^{\circ} 51'$	—
$pp = 110 : \bar{1}\bar{1}0$	36	$51 32 - 52 59$	$52 15$	$52^{\circ} 18'$
$cp = 001 : 110$	40	$57 1 - 58 50$	$57 45$	—
$cp = 00\bar{1} : 110$	32	$121 37 - 122 58$	$122 17$	$122 15$
$cr = 001 : \bar{1}01$	39	$55 12 - 57 0$	$56 8$	—
$cr = 00\bar{1} : \bar{1}01$	24	$123 7 - 124 36$	$123 50$	$123 52$
$pr = \bar{1}10 : \bar{1}01$	17	$71 42 - 72 56$	$72 27$	$72 25.5$
$pr = 110 : \bar{1}01$	8	$106 47 - 108 1$	$107 28$	$107 34.5''$

The *sulphone-sulphonate*,  $\text{EtSO}_2 \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{SO}_3\text{K} + \text{H}_2\text{O}$ , crystallised in very soluble clusters of thin scales, and fused at  $264\text{--}266^\circ$ . The quantity obtained was too small to allow of the preparation of the chloride or other derivatives.

0.1669 lost 0.0095  $\text{H}_2\text{O}$  at  $200^\circ$ .  $\text{H}_2\text{O} = 5.69$ , theory = 5.62.

0.1574 dry salt gave 0.0452  $\text{K}_2\text{SO}_4$ .  $\text{K} = 12.87$ , theory = 12.91.

*Toluene-2:4-disulphonic Acid from Orthotoluidine-4-sulphonic Acid by the Xanthate Method.*

Claus and Immel deduced the constitution of their orthotoluidine-sulphonic acid from a comparison of its bromine derivatives with those prepared by Hayduck (*Annalen*, 1874, 172, 211) from the product of reduction of orthonitrotolueneparasulphonic acid (Beilstein and Kuhlberg, *Annalen*, 1870, 155, 11). To obtain confirmation of this view by an independent method, we converted the acid into toluene-2:4-disulphonic acid by the xanthate process already described. The xanthate derivative did not separate from solution in sufficient quantity to admit of recrystallisation. As in the case of paratoluidine-3-sulphonic acid and, to a less degree, in that of orthotoluidine-5-sulphonic acid, a considerable amount of the thio-ether separated from the alkaline liquors left after hydrolysis with successive small quantities of alcoholic potash, and subsequent removal of the alcohol by distillation. The mother liquors were oxidised by permanganate, and the potassium toluenedisulphonate obtained by fractional crystallisation. The barium salt, with  $1\text{H}_2\text{O}$ , and the potassium salt, also  $1\text{H}_2\text{O}$ , of the disulphonic acid, like the chloride, melting at  $56^\circ$ , and the anilide, melting at  $187^\circ$ , agreed in every particular with the corresponding derivatives of toluene-2:4-disulphonic acid prepared from paratoluidine-2-sulphonic acid. The yield of potassium disulphonate was 81 grams, and of the thio-ether more than 42 grams from 300 grams of the amido-acid.\*

The *disulphide*  $(\text{S} \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{SO}_3\text{K})_2 + \text{H}_2\text{O}$ , was obtained only when the requisite amount of potash was added to the solution of the xanthate derivative in one quantity, and the product, after hydrolysis and removal of the alcohol, acidified with dilute sulphuric acid. This reversion to the exact details of Leuckart's process (*loc. cit.*, 218) was accompanied by an unexpectedly poor yield of the disulphonate, so that it was not followed in more than one experiment. The disulphide crystallised from water in small aggregates of minute, glistening scales, and was very soluble in water.

\* In one experiment, the diazotisation of the amido-acid was not complete, and a small amount of an azo-derivative was obtained, which crystallised from water in red needles of the composition  $\text{SO}_3\text{K} \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{N} : \text{N} \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{SO}_3\text{K} + \text{H}_2\text{O}$ .

0.1658 lost 0.0056  $\text{H}_2\text{O}$  at  $170^\circ$ .  $\text{H}_2\text{O} = 3.38$ , theory = 3.60.

0.1602 dry salt gave 0.0574  $\text{K}_2\text{SO}_4$ .  $\text{K} = 16.06$ , theory = 16.18.

The *thio-ether*,  $\text{SEt} \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{SO}_3\text{K} + 1\frac{1}{2}\text{H}_2\text{O}$ , crystallised in very small scales, was easily soluble in water, and formed an oily chloride which could not be made to crystallise.

0.248 lost 0.0236  $\text{H}_2\text{O}$  at  $180^\circ$ .  $\text{H}_2\text{O} = 9.51$ , theory = 9.09.

0.2244 dry salt gave 0.0715  $\text{K}_2\text{SO}_4$ .  $\text{K} = 14.28$ , theory = 14.44.

The *sulphone-sulphonate*,  $\text{EtSO}_2 \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{SO}_3\text{K} + \frac{1}{2}\text{H}_2\text{O}$ , was very soluble in water, and crystallised slowly from dilute alcohol in large, transparent prisms.

0.1244 lost 0.0046 at  $200^\circ$ .  $\text{H}_2\text{O} = 3.7$ , theory = 2.9.

0.1198 dry salt gave 0.034  $\text{K}_2\text{SO}_4$ .  $\text{K} = 12.72$ , theory = 12.91.

The *chloride*,  $\text{EtSO}_2 \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{SO}_2\text{Cl}$ , which crystallised in radiate groups of elongated plates from a solution in benzene that was allowed to evaporate very slowly, was very sparingly soluble in light petroleum, and melted at  $77^\circ$ .

0.1507 gave 0.0791  $\text{AgCl}$ .  $\text{Cl} = 12.98$ , theory = 12.56.

*Toluene-2:5-disulphonic Acid from Orthotoluidine-5-sulphonic Acid by the Xanthate Method.*

Toluene-2:5-disulphonic acid was recognised by Håkansson as a product of the sulphonation of toluene (*Ber.*, 1872, 5, 1088), and obtained by Klason from the thiocresolsulphonic acid prepared from diazotised orthotoluidine-5-sulphonic acid by interaction with potassium sulphide (*Ber.*, 1887, 20, 352). We prepared it, for purposes of comparison, from the amido-acid by the xanthate process already described. The *xanthate* derivative,  $\text{SO}_3\text{K} \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{S} \cdot \text{CS} \cdot \text{OEt} + \text{H}_2\text{O}$ , crystallised in very small, hexagonal scales, and was easily soluble in water.

0.4733 lost 0.0251  $\text{H}_2\text{O}$  at  $120^\circ$ .  $\text{H}_2\text{O} = 5.30$ , theory = 5.17.

0.3380 dry salt gave 0.0872  $\text{K}_2\text{SO}_4$ .  $\text{K} = 11.56$ , theory = 11.82.

The yield of the crystallised xanthate was 27 grams from 60 grams of the amido-acid, and the mother liquor was not further examined. This was hydrolysed with successive small quantities of alcoholic potash until the solution was permanently alkaline, and after removal of the alcohol by distillation, a residue was obtained which was crystallised from water. The product was not uniform, the less soluble portion giving, on analysis, numbers corresponding with those required for the percentage of potassium in the thio-ether,



$\text{SEt} \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{SO}_3\text{K}$  ( $\text{K} = 14.41-14.54$ ; theory = 14.44), whilst the more soluble portion, crystallising in clusters of very slender needles, had the composition of the expected *disulphide*  $(\text{S} \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{SO}_3\text{K})_2 + 2\text{H}_2\text{O}$ .

0.2042 lost 0.0146  $\text{H}_2\text{O}$  at  $150^\circ$ .  $\text{H}_2\text{O} = 7.15$ , theory = 6.95.

0.1896 dry salt gave 0.0672  $\text{K}_2\text{SO}_4$ .  $\text{K} = 15.89$ , theory = 16.25.

The disulphide and the liquors from which it had been crystallised were oxidised by potassium permanganate solution, and the resulting disulphonate converted into chloride, from which the barium and potassium salts were obtained subsequently by hydrolysis. The yield of crude potassium salt was 72 grams from 120 grams of the crystallised xanthate derivative.

The barium and potassium toluene-2:5-disulphonates, both with  $\text{H}_2\text{O}$ , agreed with Klason's description.

The chloride,  $\text{C}_6\text{H}_3\text{Me}(\text{SO}_2\text{Cl})_2$ , crystallised from benzene or from a mixture of benzene and light petroleum in four-sided plates arranged in groups of three or four on a common axis. It dissolved readily in benzene, chloroform, ethylic acetate, and ether, sparingly in light petroleum, and melted at  $98^\circ$ , instead of  $96^\circ$  as stated by Klason.

Mr. W. J. Pope made the following report on the crystals.

"The substance readily solidifies after melting, giving a film consisting of a confused mass of crystals which mostly shows aggregate polarisation; part of the film, however, consists of long needles, the upper faces of which are perpendicular to the acute bisectrix of a very small optic axial angle. The double refraction is positive in sign; the needles are full of pinholes and cracks."

The *anilide*,  $\text{C}_6\text{H}_3\text{Me}(\text{SO}_2\text{NHPh})_2$ , crystallised from benzene and from dilute alcohol in slender, prismatic needles, and was easily soluble in ether and in alcohol, less so in benzene, and almost insoluble in light petroleum. It melted at  $178^\circ$ .

0.3616 gave 22.1 c.c. moist nitrogen at  $23.5^\circ$  and 762 mm.

$\text{N} = 7.07$ , theory = 6.96.

The thio-ether, which formed the minor product of the hydrolysis of the xanthate derivative, was also oxidised by potassium permanganate solution, and the sulphone examined.

The *sulphone-sulphonate*,  $\text{EtSO}_2 \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{SO}_3\text{K}$ , crystallised in well-developed, anhydrous rhombs, and was less soluble in water than the potassium disulphonate.

0.2402 lost 0.0005 at  $170^\circ$ , and gave 0.0676  $\text{K}_2\text{SO}_4$ .

$\text{K} = 12.61$ , theory = 12.91.

The *chloride*,  $\text{EtSO}_2 \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{SO}_2\text{Cl}$ , was very soluble in benzene, but almost insoluble in light petroleum, and separated from a mixture of

the two as an oil, which, on spontaneous evaporation of the solvent crystallised in minute prisms melting at  $73^{\circ}$ .

0.1056 gave 0.0542 AgCl.  $\text{Cl} = 12.70$ , theory = 12.56.

Toluene-3:5-disulphonic and toluene-2:6-disulphonic acids are described incidentally in connection with orthotoluidine-3:5-disulphonic and parachlorotoluene-2:6-disulphonic acids respectively.

### III. CHLOROTOLUENESULPHONIC ACIDS.

The parachlorotoluenesulphonic acids hitherto described by Vogt and Henninger (*Ann. Chim. phys.*, 1872, [iv], 27, 130), by Hübner and Majert (*Ber.*, 1873, 6, 793), and by one of us (*Trans.*, 1892, 61, 1078) have been isolated from the mixture of acids obtained on sulphonating parachlorotoluene. As the chlorotoluene employed by Vogt and Henninger was prepared by chlorinating toluene in the presence of iodine, the  $\alpha$ - and  $\beta$ -salts described could not both be pure substances. The A and B salts obtained by one of us were recognised as probably still impure (*loc. cit.*, 1082), and, like Hübner and Majert's  $\alpha$ - and  $\beta$ -salts (with which they did not agree), differ in composition and crystalline form from the pure 1:4:3- and 1:4:2-salts prepared from the corresponding paratoluidinesulphonic acids by Sandmeyer's method. These series of salts must be regarded as no longer possessing any value other than that of illustrating the tenacity with which the isomeric barium, calcium, and lead salts respectively cling together in spite of the great difference in their solubility.

#### *Parachlorotoluene-3-sulphonic Acid.*

Parachlorotoluene-3-sulphonic acid was prepared by stirring diazotised paratoluidine-3-sulphonic acid into a lukewarm solution of cuprous chloride in hydrochloric acid, and afterwards heating the product to the boiling point; the most convenient method is to add the requisite quantity of hydrochloric acid to a solution of the potassium salt, diazotise with potassium nitrite solution without filtering, and mix the whole with the cuprous chloride solution. By this means, a considerable proportion of the substance crystallised as potassium salt from the strongly acid solution on cooling, and the remainder could be recovered from the mother liquors in the usual way.

The *barium* salt,  $(\text{C}_6\text{H}_3\text{MeCl}\cdot\text{SO}_3)_2\text{Ba} + \text{H}_2\text{O}$ , obtained either by hydrolysis of the chloride with baryta, or by precipitating a concentrated solution of the potassium salt with barium chloride, crystallised in two forms. The first consisted of thin scales, with  $1\text{H}_2\text{O}$ , the

second and more usual form of elongated, irregular, prismatic forms or, by slow crystallisation, of aggregates of rectangular prisms, with  $2\text{H}_2\text{O}$ , which became opaque on exposure to air, losing  $1\text{H}_2\text{O}$ . One part of the salt dissolved in about 10 parts of water at  $15^\circ$ .

- 0.4968, prisms, gave  $0.0322 \text{H}_2\text{O}$  at  $200^\circ$ .  $\text{H}_2\text{O} = 6.48$ , theory =  $6.16$ .  
 0.326, effloresced prisms, gave  $0.01 \text{H}_2\text{O}$  at  $200^\circ$ .  $\text{H}_2\text{O} = 3.07$ , theory =  $3.18$ .  
 0.45, scales, gave  $0.0142 \text{H}_2\text{O}$  at  $200^\circ$ .  $\text{H}_2\text{O} = 3.15$ .  
 0.4358 dry salt gave  $0.1856 \text{BaSO}_4$ .  $\text{Ba} = 25.03$ , theory =  $25.00$ .

The *potassium* salt,  $\text{C}_6\text{H}_3\text{MeCl}\cdot\text{SO}_3\text{K} + \text{H}_2\text{O}$ , crystallised in well defined, rectangular plates often aggregated together, forming large crystals, or occasionally from slightly alkaline solutions as a mass of slender needles which slowly changed into the prismatic form when allowed to remain in the mother liquor.

- 0.4416, needles, lost  $0.0306 \text{H}_2\text{O}$  at  $180^\circ$ .  $\text{H}_2\text{O} = 6.93$ . } theory =  $6.85$ .  
 0.3142, plates, lost  $0.0216 \text{H}_2\text{O}$  at  $180^\circ$ .  $\text{H}_2\text{O} = 6.87$ . }  
 0.2926 dry salt gave  $0.1038 \text{K}_2\text{SO}_4$ .  $\text{K} = 15.91$ , theory =  $15.95$ .

The *sodium* salt,  $\text{C}_6\text{H}_3\text{MeCl}\cdot\text{SO}_3\text{Na} + \text{H}_2\text{O}$ , crystallised in very slender needles, or from more dilute and slightly alkaline solutions as a mixture of needles with well-defined, flat prisms which grew at the expense of the former until prisms alone were present.

- 0.518, prisms, lost  $0.039 \text{H}_2\text{O}$  at  $180^\circ$ .  $\text{H}_2\text{O} = 7.53$ . } theory =  $7.30$ .  
 0.4324, needles, lost  $0.0314 \text{H}_2\text{O}$  at  $180^\circ$ .  $\text{H}_2\text{O} = 7.26$ . }  
 0.401 dry salt gave  $0.1256 \text{Na}_2\text{SO}_4$ .  $\text{Na} = 10.14$ , theory =  $10.06$ .

The *chloride*,  $\text{C}_6\text{H}_3\text{MeCl}\cdot\text{SO}_2\text{Cl}$ , which was very soluble in benzene and in ether, crystallised from light petroleum in large, elongated, hexagonal plates, often 2—3 mm. thick and 25—30 mm. long, and melted at  $56^\circ$ .

- 0.1118 gave  $0.1433 \text{AgCl}$ .  $\text{Cl} = 31.70$ , theory =  $31.55$ .

The *amide* crystallised from dilute alcohol in flat, dull looking plates, shaped like spear heads, and melted at  $156^\circ$ .

The *anilide*,  $\text{C}_6\text{H}_3\text{MeCl}\cdot\text{SO}_2\text{NHPh}$ , crystallised from alcohol in prisms which were much smaller than those of the 1:4:2-isomeride, and only about one-tenth as soluble in the boiling solvent. It was almost insoluble in light petroleum, but about twice as soluble in hot benzene as the 1:4:2-isomeride. It melted at  $188^\circ$ , and a mixture in equal proportions with the 1:4:2-isomeride, after fusion and solidification, melted at  $161$ — $165^\circ$ .

- 0.5508 gave  $24.1 \text{c.c.}$  moist nitrogen at  $19^\circ$  and 759 mm.  
 $\text{N} = 5.12$ , theory =  $4.97$ .

Mr. W. J. Pope examined the crystals and reported as follows.

"The crystals consist of small, colourless, transparent, monosymmetric prisms or needles showing the forms  $p\{110\}$  and  $q\{011\}$ ; the angle  $110:\bar{1}10$  is  $66^\circ 40'$ . The extinction through the form  $p\{110\}$  is oblique to the zone axis, and one optic axis can be observed emerging just outside the microscope field. After melting, the substance solidifies readily to a rather opaque film, showing a few broad, flat plates amongst the rather confused crystalline mass; these are nearly perpendicular to the acute bisectrix of a large optic axial angle. The double refraction is negative in sign, and the film cracks very much during cooling."

*Parachlorotoluene-2-sulphonic Acid.*

Parachlorotoluene-2-sulphonic acid was obtained by stirring diazotised paratoluidine-2-sulphonic acid into a lukewarm solution of cuprous chloride in hydrochloric acid and afterwards heating the product to boiling point, following the method already described.

The barium salt,  $(C_6H_3MeCl \cdot SO_3)_2Ba + H_2O$ , was first described by Jennsen (*Annalen*, 1874, 172, 239), who obtained it in small scales, with  $1H_2O$ . It was easily prepared by precipitating a solution of the potassium salt with barium chloride, as one part requires about one hundred parts of water for solution at  $15^\circ$ . The crystalline form seemed to depend largely on the temperature. When crystallised from hot solutions, the salt separated only in lustrous scales, but when the temperature, during cooling, fell to about  $50^\circ$  the crystals were of a mixed appearance owing to the deposition of small, prismatic aggregates, and frequently the salt could be made to separate exclusively in the latter form by employing solutions of such a strength that crystallisation did not begin until the temperature had fallen below this point. Either form could be converted into the other by observing these conditions, and the only difference noticed between them, apart from their appearance, was the fact that the crystalline aggregates contained slightly less water of crystallisation (2.85—3.1 per cent.) than the scales.

0.533, aggregates, lost  $0.016 H_2O$  at  $200^\circ$ .  $H_2O = 3.00$ , theory = 3.18.

0.518, scales, lost  $0.017 H_2O$  at  $200^\circ$ .  $H_2O = 3.28$ .

0.501 dry salt gave  $0.213 BaSO_4$ .  $Ba = 24.99$ ,  $Ba = 25.00$ .

The *potassium* salt,  $C_6H_3MeCl \cdot SO_3K$ , crystallised in radiate groups of long, anhydrous, prismatic needles, and was easily soluble in water.

0.482 lost  $0.0012$  at  $180^\circ$  and gave  $0.1708 K_2SO_4$ .

$K = 15.88$ , theory = 15.95.



The *sodium* salt,  $C_6H_3MeCl \cdot SO_3K + \frac{1}{2}H_2O$ , crystallised from water in easily soluble, rectangular, lustrous scales.

0.4584 lost 0.0178  $H_2O$  at  $180^\circ$ .  $H_2O = 3.88$ , theory = 3.80.

0.4406 dry salt gave 0.137  $Na_2SO_4$ .  $Na = 10.07$ , theory = 10.06.

The *chloride*,  $C_6H_3MeCl \cdot SO_2Cl$ , when first obtained, was an oil at the ordinary temperature, and was easily soluble in benzene, ether, or light petroleum. On cooling in a freezing mixture, it crystallised in large, four-sided, thin, elongated plates, which when freed from adhering oil, fused, again cooled, and the process repeated four or five times, were found to melt constantly at  $24^\circ$ .

0.2704 gave 0.3446  $AgCl$ .  $Cl = 31.52$ , theory = 31.55.

The amide crystallised from dilute alcohol in long, slender needles, and melted at  $142^\circ$ . That prepared by Heffter from paratoluidine-2-sulphonamide melted at  $138^\circ$  (*Annalen*, 1883, 221, 209).

The *anilide*,  $C_6H_3MeCl \cdot SO_2NHPh$ , crystallised from alcohol in plates which not infrequently were aggregated together, forming massive crystals. It dissolved easily in alcohol or ether, slightly in benzene, very sparingly in light petroleum, and melted at  $144^\circ$ .

0.4169 gave 18.8 c.c. moist nitrogen at  $20^\circ$  and 751 mm.

$N = 5.21$ , theory = 4.97.

Mr. W. J. Pope examined the crystals and reported as follows.

"The crystals are large, transparent plates, belonging to the monosymmetric system; they are very brittle and possess a glassy lustre. The dominant form is the pinacoid  $a\{100\}$ , the faces of which give good reflections; the form  $q\{011\}$  is smaller and the faces are not so plane as those of  $a\{100\}$ . The prism  $p\{110\}$  is small, and the pinacoid  $b\{010\}$  is only rarely observed.

"The optic axial interference figure is observed on microscopic examination through  $a\{100\}$ , the acute bisectrix being nearly perpendicular to this face; the axis  $b$  is the obtuse bisectrix, the optic axial angle is fairly large, and there is marked inclined optic axial dispersion. The double refraction is negative in sign.

"After melting, the substance solidifies readily, crystallising from centres in broad plates, which are mostly perpendicular to the bisectrix of a large optic axial angle; the bisectrix is of positive double refraction

"*Crystalline System*.—Monosymmetric.

$$a : b : c = 1.5711 : 1 : 0.9254.$$

$$\beta = 74^\circ 51'5''.$$

"*Forms observed*.— $a\{100\}$ ,  $b\{010\}$ ,  $p\{110\}$ , and  $q\{011\}$ .

"The following angular measurements were obtained.



Angle.	Number of observations.	Limits.	Mean.	Calculated.
$ap=100:110$	32	$55^{\circ}17' - 57^{\circ}40'$	$56^{\circ}36'$	—
$bp=010:110$	24	$32\ 11 - 34\ 31$	$33\ 17$	$33^{\circ}24'$
$pp=110:110$	18	$65\ 52 - 67\ 28$	$66\ 38$	$66\ 48$
$pp=110:110$	9	$112\ 36 - 114\ 1$	$113\ 24$	$113\ 12$
$bq=010:011$	25	$47\ 42 - 49\ 13$	$48\ 30$	$48\ 13\cdot5$
$qq=011:011$	29	$95\ 56 - 97\ 39$	$96\ 41$	$96\ 27$
$qq=011:011$	38	$82\ 47 - 84\ 22$	$83\ 33$	—
$aq=100:011$	31	$77\ 45 - 79\ 54$	$78\ 46$	—
$pq=110:011$	12	$47\ 59 - 49\ 26$	$48\ 47$	$48\ 26\cdot5$
$pq=110:011$	7	$62\ 8 - 64\ 15$	$63\ 3$	$63\ 19\cdot5$ "

As the respective chlorides and anilides of the two parachloro-toluenesulphonic acids exhibited marked differences in solubility and melting points, experiments were made to investigate the possibility of separating the 1:4:3-compound from mixtures containing known proportions of the two isomerides.

The 1:4:3-chloride was dissolved in its isomeride by fusion, and the mixture allowed to crystallise either at the ordinary temperature or, when necessary, in a freezing mixture, the crystalline mass in the latter case being allowed to assume a temperature of  $15^{\circ}$  to remove the more fusible portion before filtration. Four proportions were used, namely, 5 grams of the 1:4:3-chloride to 5, 10, 15 and 20 grams respectively of the 1:4:2-compound; the crystals separated weighed approximately 3, 1, 0.7, and 0.3 grams, and the melting points were  $39-40^{\circ}$ ,  $28^{\circ}$ ,  $22-23^{\circ}$  and  $20-21^{\circ}$  respectively. These experiments were not carried further, and may serve to explain the inconclusive results obtained by one of us in dealing with the chlorides obtained from salts which must now be regarded as mixtures of the two isomerides (*loc. cit.*, 1081).

The mixed anilides were dissolved in the minimum quantity of boiling alcohol, 3 grams of the 1:4:3-compound being used with 3, 6, 9, and 12 grams of the 1:4:2-derivative. The first mixture dissolved in 70 c.c. and the last in 85 c.c. of hot alcohol. Two crystalline deposits were obtained in each case, the first in striated, irregular, elongated prisms while the solution was warm, the second in small, well-developed prisms after the mother liquor had been allowed to remain overnight. The crystals deposited were found to have the following approximate weights and melting points: (1) 2 grams, melting at  $172-173^{\circ}$ ; 1 gram melting at  $169-170^{\circ}$ ; (2) 2.5 grams, melting at  $163-164^{\circ}$ ; 2 grams melting at  $159^{\circ}$ ; (3) 2.5 grams, melting at  $158^{\circ}$ ; 4 grams melting at  $155-156^{\circ}$ ; (4) 3.5 grams, melting at  $154-156^{\circ}$ ; 6.5 grams melting at  $150-151^{\circ}$ , a further separation in this case being obtained by adding water to the hot

mother liquor, whereby an additional 4.5 grams was obtained as a crystalline powder melting at 144—145°. The first two portions obtained in the fourth experiment were recrystallised, and after seven repetitions gave 0.6 gram melting at 186°. The method, although it indicated the presence of the 1:4:3-isomeride in mixtures containing even as little as 10 per cent. by the fact that the first crop of crystals had a melting point higher than that of the 1:4:2-isomeride, was evidently of little value as a means of estimating its amount.

*Orthochlorotoluene-4-sulphonic Acid.*

Paysan obtained an acid which he regarded as orthochlorotoluene-4-sulphonic acid by heating orthochlorotoluene-4-sulphonamide, prepared from orthotoluidine-4-sulphonamide, with hydrochloric acid at 150° during several hours. Although the amide had the same properties as that described below, the barium and potassium salts are stated to be anhydrous, and the chloride an uncrystallisable oil, even at low temperatures (*Annalen*, 1883, 221, 212).

We prepared the acid by stirring diazotised orthotoluidine-4-sulphonic acid into a lukewarm solution of cuprous chloride in hydrochloric acid, and afterwards heating the product to boiling, following the method already described.

The *barium* salt,  $(C_6H_3MeCl \cdot SO_3)_2Ba + H_2O$ , crystallised in small, thin, elongated scales, and was fairly soluble in water.

0.3108 lost 0.0108  $H_2O$  at 180°.  $H_2O = 3.47$ ; theory = 3.18.

0.3 dry salt gave 0.1277  $BaSO_4$ .  $Ba = 25.02$ ; theory = 25.00.

The *potassium* salt,  $C_6H_3MeCl \cdot SO_3K + \frac{1}{2}H_2O$ , crystallised in large, elongated, hexagonal plates, or from more concentrated solutions in glistening scales, and was moderately soluble in water.

0.4874 lost 0.0168  $H_2O$  at 180°.  $H_2O = 3.45$ ; theory = 3.55.

0.4706 dry salt gave 0.1668  $K_2SO_4$ .  $K = 15.88$ ; theory = 15.95.

The *sodium* salt,  $C_6H_3MeCl \cdot SO_3Na + \frac{1}{2}H_2O$ , crystallised in thicker but smaller plates than the potassium salt, and was about equally soluble in water.

0.455 lost 0.0186  $H_2O$  at 180°.  $H_2O = 4.09$ ; theory = 3.79.

0.4364 dry salt gave 0.1354  $Na_2SO_4$ .  $Na = 10.01$ ; theory = 10.06.

The *chloride*,  $C_6H_3MeCl \cdot SO_2Cl$ , dissolved easily in the usual solvents, and, on slow evaporation of its solution in light petroleum, crystallised in long, massive prisms, often clustered together in divergent, fan-like rays composed of from three to six crystals. It melted at 37°.

0.1412 gave 0.1776  $AgCl$ .  $Cl = 31.11$ ; theory = 31.55.

The amide crystallised from dilute alcohol in long, slender needles, and melted at  $134^{\circ}$ .

The *anilide*,  $C_6H_3MeCl \cdot SO_2NHPh$ , dissolved easily in benzene, alcohol, ether, chloroform, acetone, and ethylic acetate, but sparingly in light petroleum, and crystallised best from alcohol in prisms, which at first had the appearance of hexagonal plates. It melted at  $96^{\circ}$ .

0.4309 gave 19 c.c. moist nitrogen at  $18^{\circ}$  and 755 mm.

$N = 5.15$  ; theory = 4.97.

Mr. W. J. Pope examined the crystals, and reported as follows.

"The crystals consist of small, brown, rhomb-shaped plates; they are lustrous, transparent, and very brittle, and the extinction bisects the angles of the rhomb. No optic axial interference figure could be observed. After melting, the cooled mass solidifies very slowly, giving a film showing aggregate polarisation."

#### *Orthochlorotoluene-5-sulphonic Acid.*

The salts of this acid have been described (Trans., 1892, 61, 1040, 1073). As the amide melted at  $128^{\circ}$ , within  $6^{\circ}$  of its isomeride, the *anilide*,  $C_6H_3MeCl \cdot SO_2NHPh$ , was prepared for purposes of comparison. It resembled the 1:2:4-isomeride in its solubility in the usual solvents, crystallising from most of them in thin, irregular scales. From alcohol, it crystallised in small, well developed prisms melting at  $92^{\circ}$ . On fusion with an equal proportion of the 1:2:4-anilide, a mixture was formed which, after solidification, melted constantly at  $75-76^{\circ}$ .

0.4531 gave 19.6 c.c. moist nitrogen at  $20^{\circ}$  and 755 mm.

$N = 5.02$  ; theory = 4.97.

Mr. W. J. Pope made the following report on the crystals.

"The crystals consist of small, brown, transparent, rhomb-shaped plates belonging to the anorthic system; the extinction through the large face is oblique, and this face is nearly perpendicular to the acute bisectrix of a large optic axial angle; the double refraction is negative in sign, and the optic axial dispersion marked. After melting and cooling, the solid film is found to consist of brush-like crystalline forms containing a number of broad individual flakes; some of the latter are nearly perpendicular to an optic axis."

#### IV. CHLOROTOLUENEDISULPHONIC ACIDS.

The chlorotoluenedisulphonic acids described in this section were obtained by heating the isomeric potassium chlorotoluenesulphonates at  $150^{\circ}$  during 2 hours with anhydrosulphuric acid containing sufficient dissolved anhydride to effect the sulphonation. The products in

each case, after cooling, were poured on to crushed ice, mixed with alcohol to remove as much potassium hydrogen sulphate as possible, and the filtrates, after removal of the greater part of the alcohol, converted into barium salts. These, after fractional crystallisation to a limited extent, were converted into potassium salts, care being taken to extract the barium sulphate residues obtained during neutralisation, by boiling them with dilute potassium carbonate solution. As excess of alkali seemed to impede the separation of the isomeric salts, it was in every case removed by carefully neutralising with sulphuric acid, and precipitating the potassium sulphate with alcohol. Preliminary experiments with the potassium parachlorotoluenesulphonates seemed to indicate that 20 per cent. anhydrosulphuric acid effected complete sulphonation; this, however, was not the case, as some 25 per cent. of the monosulphonate was recovered unchanged. As the object of the investigation was the quantitative determination of the constituents in the mixture of monosulphonic acids obtained from toluene, the sulphonation would have been repeated with 30 per cent. anhydrosulphuric acid, but for the tedious nature of the separation; the results obtained, however, may be regarded as sufficiently accurate for the purpose, even though the conversion into disulphonic acids was incomplete.

*Sulphonation of Potassium Parachlorotoluene-3-sulphonate.*

After preliminary trials, 50 grams of potassium parachlorotoluene-3-sulphonate were sulphonated, and the product separated by fractional crystallisation into 29 grams of potassium 3:5-disulphonate, 13 grams of potassium 2:5-disulphonate, and 18 grams of residual salt. A more systematic examination was then undertaken. For this purpose, 100 grams of the dry potassium salt were heated with 170 grams of 20 per cent. anhydro-acid, and the product converted into barium salt as described. The earlier and less soluble portions separated were usually ill-defined or gelatinous, the later and more soluble fractions were in scales mixed to a greater or less extent with the foregoing, and difficult to separate. These and the mother liquors were converted into potassium salts and fractionally crystallised. The less soluble barium salts consisted almost entirely of potassium 2:5-disulphonate, crystallising with  $2\text{H}_2\text{O}$  in aggregates of small scales; the more soluble barium salts, a mixture of this with potassium 3:5-disulphonate, crystallising with  $6\text{H}_2\text{O}$  in efflorescent needles; whilst the mother liquor gave potassium 3:5-disulphonate and unchanged monosulphonate. The fractionation of these salts was fairly easy, and as a rule alternate separations were obtained, although the two parachlorotoluenedisulphonates were about equally soluble in water. To remove the last of the disulphonate from the mother



liquors, alcohol was added in quantities up to 50 per cent., the monosulphonate being left in the final liquors, whether aqueous or alcoholic. Eventually, the following amounts of the various potassium salts, dried at 160°, were accounted for.

	Isolated as salt.	Calculated from chlorides.*	Total.
Parachlorotoluene-3:5-disulphonate ...	69	5	74
„ -2:5-disulphonate ...	37	2	39
„ -monosulphonate ...	12	9	21

Deducting the monosulphonate, it follows that, taking the weight of the salts actually isolated and that calculated from the chlorides, 113 grams of disulphonate were accounted for instead of the theoretical yield of 117 grams, and that the 2:5- and 3:5-disulphonates were present approximately in the proportion of one to two.

The identity of both the disulphonates, and of the recovered monosulphonate was established by conversion into the respective chlorides and anilides, and only the products from the monosulphonate need be referred to in detail. The chloride from the monosulphonate (13 grams), on repeated crystallisation, gave 3 grams melting at 49—50°. Both this, and the residue (9 grams) were converted into anilide, and, without recrystallisation, that from the former melted at 183—184°, and that from the latter (7 grams) melted at 177—179°, thus proving the uniformity of the recovered salt.

#### *Sulphonation of Potassium Parachlorotoluene-2-sulphonate.*

After preliminary experiments, 50 grams of parachlorotoluene-2-sulphonate were sulphonated as described, and the product converted into potassium salt in the usual way. On fractional crystallisation, 25 grams of 2:6-disulphonate in anhydrous scales, 20 grams (dried at 160°) of disulphonate in scales containing about 6 per cent. of water of crystallisation, and 15 grams of residual salt were obtained. The hydrated salt seemed to be uniform, as crystallisation from water did not alter its appearance or appreciably affect the percentage of water, which, however, was too high for a monhydrated compound. Converted into chloride, 10 grams of the dry salt gave 6 grams of crude substance from which nothing but parachlorotoluene-2:6-disulphonic chloride, melting at 108°, was isolated—a result which,

\* The “chlorides” here mentioned were obtained from mixtures of the salts left after as much as possible of the monosulphonate and of the 3:5- and 2:5-disulphonates had been removed and isolated by fractional crystallisation. As a rule, the yield of chloride was about 60—75 per cent. of the theoretical. Although differences were noticed in the readiness with which some of the salts, particularly the 2:5-disulphonate, interacted with phosphorus pentachloride, the proportions obtained in separations effected by means of the chlorides were assumed to be, for purposes of calculation, those in which the isomeric salts existed in the mixture.



at the time, led to the conclusion being drawn that only one disulphonic acid had been formed (Proc., 1895, 11, 153).

A repetition of the experiment resulted in the separation of 33 grams of 2:6-disulphonate in anhydrous scales, 7 grams of 2:5 disulphonate in scales with  $2\text{H}_2\text{O}$ , 8 grams of disulphonate in scales containing about 6.5 per cent. of water of crystallisation, and 13 grams of residual material. Examination of the chloride obtained from the approximately monohydrated salt, showed that the sparingly soluble 2:5-isomeride melting at  $144^\circ$  was present, in addition to the 2:6-derivative melting at  $109^\circ$ , and the failure to detect it on the previous occasion is to be referred to the comparatively poor yield of chloride obtained from the 2:5-salt, unless the interaction with phosphorus pentachloride is prolonged.

A third experiment was then made, in which 100 grams of the dry salt were heated with 170 grams of 20 per cent. anhydrosulphuric acid, and the product converted into barium salt as described. The earlier and less soluble portions separated were mainly granular, the later and more soluble were in scales, but as fractional crystallisation seemed to lead to little result, these and the mother liquors were converted respectively into potassium salts. The less soluble barium salts gave chiefly the 2:5-disulphonate, together with 3 grams of sparingly soluble potassium sulphone-sulphonate, the more soluble barium salts, a mixture of the 2:6-disulphonate with that crystallising with about 6 per cent.  $\text{H}_2\text{O}$ , and some unchanged monosulphonate, while the mother liquors gave 2:6-disulphonate and the remainder of the monosulphonate. Eventually the following quantities of the various potassium salts, dried at  $160^\circ$ , were accounted for.

	Isolated as salt.	Calculated from chlorides.*	Total.
Parachlorotoluene-2:6-disulphonate.....	64.5	10	74.5
„ -2:5-disulphonate.....	14.5	9	23.5
„ -sulphone-sulphonate...	3	—	3
„ -monosulphonate .....	13	12	25

Deducting the 25 grams of monosulphonate and the 3 grams of sulphone-sulphonate, it follows that 98 grams of disulphonate were accounted for instead of the theoretical yield of 108 grams, and that the 2:5- and 2:6-disulphonates were present in approximately the proportion of one to three.

The fractional crystallisation was difficult and tedious in this case. The greater part of the 2:6-salt was separated without difficulty, but the remainder, amounting to about one-fourth of the whole, crystallised along with 2:5-salt in hydrated, small scales, more soluble than either of the isomerides. Repeated fractional treatment of the aqueous solu-

\* See footnote, p. 767.

tion with alcohol gave fractions which usually contained more than 6 per cent. of water, whilst those obtained by concentrating the alcoholic mother liquor were less hydrated than this. Such fractions, on crystallisation from water, were partially resolved into small quantities of the 2:5- and 2:6-salts respectively, with a residue consisting approximately of monhydrated salt, which by repetitions of the process could be further resolved until a residue of 13 grams (dried at  $160^{\circ}$ ) was obtained which resisted further treatment. Determinations of the water of crystallisation had to be made in each case, as the appearance of the various fractions gave little clue to their nature. This 13 grams of hydrated salt was converted into chloride giving 6.5 grams which was mainly the 2:6-derivative, although it contained a small quantity of the 2:5-chloride. The residues were therefore worked up, and an additional 2.5 grams of chloride, chiefly the 2:5-compound, obtained from the recovered salt. Fractional crystallisation from benzene effected a separation of the isomerides, and the amounts obtained were 3.5 grams of the sparingly soluble 2:5-chloride melting at  $143\text{--}144^{\circ}$ , and 5.2 grams of the easily soluble 2:6-isomerides; quantities in the approximate ratio of two to three. For the purposes of calculation, it was assumed that the salt contained the disulphonates in this proportion.

The identity of the disulphonates and of the monosulphonate was confirmed by conversion into the corresponding chlorides and anilides. The products from the monosulphonate proved this to be unchanged 1:4:2-salt. The chloride was an oil, from which 6 grams, melting at  $23\text{--}24^{\circ}$ , were obtained by crystallisation in a freezing mixture. Both this and the residual oil were converted into anilides, which melted at  $144^{\circ}$ , and  $141\text{--}142^{\circ}$  respectively, the weight of anilide of the latter melting point, obtained from the oil, being 7 grams.

*Parachlorotoluene-2:6-disulphonic acid.*—The potassium parachlorotoluenedisulphonate crystallising in anhydrous scales was isomeric with the salts obtained from the two paratoluidinedisulphonic acids by Sandmeyer's method, and has not been described hitherto.

The *barium* salt,  $\text{C}_6\text{H}_2\text{MeCl}(\text{SO}_3)_2\text{Ba} + 3\frac{1}{2}\text{H}_2\text{O}$ , obtained from the chloride by hydrolysis with baryta, crystallised from water in sparingly soluble, small prisms.

0.2969 lost 0.0367  $\text{H}_2\text{O}$  at  $200^{\circ}$ .  $\text{H}_2\text{O} = 12.36$ , theory = 13.00.

0.2602 dry salt gave 0.1454  $\text{BaSO}_4$ .  $\text{Ba} = 32.85$ , theory = 32.50.

The *potassium* salt,  $\text{C}_6\text{H}_2\text{MeCl}(\text{SO}_3\text{K})_2$ , crystallised from water in fairly soluble, anhydrous scales.

0.3206 lost 0.0005 at  $200^{\circ}$  and gave 0.1532  $\text{K}_2\text{SO}_4$

$\text{K} = 21.41$ , theory = 21.52.

The *chloride*,  $\text{C}_6\text{H}_2\text{MeCl}(\text{SO}_2\text{Cl})_2$ , crystallised either from benzene, or

from a mixture of benzene and light petroleum, in large prisms, dissolved easily in benzene, less readily in ether, sparingly in light petroleum, and melted at  $108^{\circ}$ .

0.0984 gave 0.13 AgCl.  $\text{Cl} = 32.81$ , theory = 32.92.

Mr. W. J. Pope made the following report on the crystals.

"The crystals deposited from a mixture of benzene and petroleum are large, pale yellow plates belonging to the monosymmetric system (Fig. 5); they are very brilliant and transparent, and possess a calcite-like lustre. The pinacoid  $b\{010\}$  is dominant, and the form  $p\{110\}$  is the next largest in size; the pinacoid  $c\{001\}$  is also usually large, whilst  $q\{011\}$  is in general small. All these forms give fairly good results on measurement, but there is usually present in the zone  $[011 : \bar{1}10]$  a form  $\omega\{hkl\}$  the faces of which are striated by lines parallel to the zone-axis; these striations are so well marked that no measurements could be obtained from the faces.

"There is a good cleavage parallel to  $b\{010\}$ , but no interference figure could be observed.

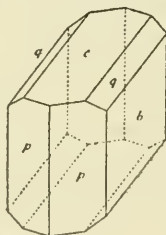
"*Crystalline System.*—Monosymmetric.

$$a : b : c = 0.4943 : 1 : 0.6533.$$

$$\beta = 74^{\circ} 1'.$$

"*Forms observed.*— $b\{010\}$ ,  $c\{001\}$ ,  $p\{110\}$ , and  $q\{011\}$ .

FIG. 5.



"The following angular measurements were obtained.

Angle.	Number of observations.	Limits.	Mean.	Calculated.
$cp = 001 : 110$	14	$75^{\circ}29' - 75^{\circ}41'$	$75^{\circ}35'$	$75^{\circ}36'$
$cp = 00\bar{1} : 110$	10	$104\ 16 - 104\ 29$	$104\ 23$	$104\ 24$
$cq = 001 : 011$	18	$32\ 1 - 32\ 20$	$32\ 10$	$32\ 8$
$bq = 010 : 011$	27	$57\ 44 - 58\ 1$	$57\ 52$	—
$bp = 010 : 110$	34	$64\ 31 - 64\ 40$	$64\ 35$	—
$pp = 110 : \bar{1}\bar{1}0$	16	$50\ 45 - 51\ 0$	$50\ 51$	$50\ 50$
$pq = 110 : 01\bar{1}$	20	$88\ 54 - 89\ 8$	$88\ 59$	—
$pq = 110 : 0\bar{1}1$	15	$90\ 51 - 91\ 7$	$91\ 0$	$91\ 1$
$pq = 110 : 011$	8	$63\ 52 - 64\ 4$	$63\ 57$	$63\ 58$
$pq = 110 : 0\bar{1}\bar{1}$	4	$115\ 57 - 116\ 11$	$116\ 4$	$116\ 2''$

The *anilide*,  $C_6H_2MeCl(SO_2NHPh)_2$ , crystallised from benzene and from dilute alcohol in small, lustrous scales, dissolved sparingly in benzene, readily in alcohol, and melted at  $188^\circ$ .

0.3899 gave 20.2 c.c. moist nitrogen at  $18.5^\circ$  and 760 mm.

$N = 6.08$ , theory = 6.41.

This acid can have only one of two formulæ; it must be either the 2:6- or the 2:3-disulphonic acid, and although no experimental means exist at present for discriminating between these alternatives, the former is much the more probable. Parabromotoluene, like the chloro-derivative, yields chiefly the 1:4:2-monosulphonic acid, as already stated, and one disulphonic acid according to Kornatzki (*Annalen*, 1883, 221, 200). The latter is commonly regarded as the 2:6-derivative (compare Klason, *loc. cit.*), although Kornatzki did not discuss its constitution, and merely drew attention to the fact that the toluene-disulphonic acid obtained from it by reduction with sodium amalgam was different from any of the isomeric acids known at the time.

In view of Kornatzki's results, the potassium parachlorotoluene-disulphonate was reduced in aqueous solution by 2 per cent. sodium amalgam. The product, after neutralisation with sulphuric acid, was evaporated to the crystallising point, and the sulphate precipitated by the addition of twice the volume of alcohol; the filtrate, again evaporated to the crystallising point, gave a copious precipitate of the toluenedisulphonate on adding ten times the volume of alcohol; this was converted into the chloride, which proved to be identical with that described by Kornatzki. The barium salt crystallised from concentrated hot solutions in rhombs, with  $2H_2O$ , but at temperatures below  $50^\circ$  in radiate, glistening, flat needles, with  $4H_2O$ , and was very soluble in water; the potassium salt crystallised in equally soluble, anhydrous, flat prisms.

The chloride,  $C_6H_3Me(SO_2Cl)_2$ , crystallised from benzene in elongated prisms, was easily soluble in benzene, ether, and chloroform, very sparingly in light petroleum, and melted at  $88^\circ$ .

Mr. W. J. Pope examined the crystals and reported as follows.

"The crystals consist of small, colourless prisms belonging to the monosymmetric system; they are very brittle, and the prism  $p\{110\}$  is dominant. This form gives fairly good results on measurement, as does also the dome  $q\{011\}$ , the faces of which, although small, are very brilliant. The pinacoid  $b\{010\}$  is but rarely observed. Microscopic examination through  $p\{110\}$  shows one optic axis of a biaxial substance emerging just outside the field of vision.

"After melting, the material solidifies readily, giving a very transparent film containing a few air-holes; the film cracks a little on cooling and consists partly of large, crystalline individuals, the top faces of



which are nearly perpendicular to the acute bisectrix of a large optic axial angle. The double refraction is negative in sign.

" *Crystalline System.*—Monosymmetric.

$$a : b : c = 0.7509 : 1 : 0.9243.$$

$$\beta = 46^\circ 36'.$$

" *Forms observed.*— $b\{010\}$ ,  $p\{110\}$ , and  $q\{011\}$ .

" The following angular measurements were obtained.

Angle.	Number of observations.	Limits.	Mean.	Calculated.
$bp = 010 : 110$	16	$60^\circ 7' - 61^\circ 59'$	$61^\circ 15'$	$61^\circ 23'$
$pp = 110 : 110$	39	$56^\circ 5' - 58^\circ 12'$	$57^\circ 14'$	—
$pp = 110 : 110$	11	$121^\circ 47' - 123^\circ 16'$	$122^\circ 35'$	$122^\circ 46'$
$bq = 010 : 011$	15	$55^\circ 4' - 57^\circ 38'$	$56^\circ 21'$	$56^\circ 7'$
$qq = 011 : 011$	32	$65^\circ 52' - 69^\circ 7'$	$67^\circ 46'$	—
$qq = 011 : 011$	18	$111^\circ 32' - 113^\circ 4'$	$112^\circ 29'$	$112^\circ 14'$
$pq = 110 : 011$	14	$39^\circ 1' - 40^\circ 57'$	$39^\circ 51'$	— "

The *anilide*,  $C_6H_3Me(SO_2NHPh)_2$ , which crystallised from dilute alcohol in aggregates of diamond-shaped prisms, and from benzene in minute prisms, was easily soluble in alcohol, acetone, and ether, sparingly in chloroform and benzene, and melted at  $162^\circ$ .

0.4958 gave 30.5 c.c. moist nitrogen at  $23^\circ$  and 762 mm.

$$N = 7.11, \text{ theory} = 6.96.$$

*Sulphonation of the mixed Potassium Parachlorotoluenesulphonates obtained from Parachlorotoluene.*

After a trial experiment, parachlorotoluene (100 grams) was heated with 20 per cent. anhydrosulphuric acid (650 grams) at  $150^\circ$  during 2 hours, and the product converted into barium salt and subsequently into potassium salt. As the result of fractional crystallisation, the following potassium salts (dried at  $160^\circ$ ) were isolated: 2:6-disulphonate, 113 grams; 2:5-disulphonate, 21 grams; 3:5-disulphonate, 8 grams; disulphonate crystallising in scales with about 6 per cent. of water, 10 grams; mixed disulphonates, 32 grams; residual salts, 35 grams; making a total of 219 grams instead of the theoretically possible yield of 268 grams. The separation was not carried further, because the results were open to the objection that toluenesulphonic acids on the one hand, and their potassium salts on the other, might not yield disulphonic acids in the same proportion, and these details are quoted merely to show that they correspond very fairly with those which follow.

A third experiment was made, in which 100 grams of parachloro-



toluene were sulphonated by heating with 315 grams of pure sulphuric acid at the temperature of the water bath, and the product converted into potassium salt in the usual way. The various separations and the final liquor, containing a small amount of inorganic salt which could not be separated easily, were dried at  $180^{\circ}$ , and the product, weighing 197 grams (theoretically 193 grams), was heated with 340 grams of 20 per cent. anhydrosulphuric acid at  $150^{\circ}$  during 2 hours. The barium salt was separated into eight fractions, of which the first four were comparatively small in amount, and consisted of a mixture of scales and crystalline aggregates, the next three were large, and consisted chiefly of microscopic hair-like needles, and the last was the mother liquor. The potassium salts were obtained from these, and by good fortune it was found that the first three barium salt fractions gave little else than the 2:5-disulphonate, which, although the least soluble of the three isomerides, is difficult to separate in the presence of the 2:6-derivative, as already explained. The fourth, fifth, sixth, and seventh fractions of the barium salt gave mixtures of the three isomeric disulphonates (from which 4 grams only of the 2:5-disulphonate was isolated) with some monosulphonate, whilst the mother liquor gave 8 grams only of the mixed 2:6- and 3:5-disulphonates together with monosulphonate and some potassium ethyl sulphate, doubtless derived from the alcohol employed to remove potassium hydrogen sulphate before neutralisation.

Although the necessity of separating the 2:5- and 2:6-disulphonates from the mixed salts crystallising with about 6 per cent. of water was avoided, a similar difficulty was met with in dealing with a number of separations in scales from the various mother liquors. These seemed to be mixtures of monosulphonate with the 2:6- and 3:5-disulphonates ( $K = 18.05 - 19.54$ ;  $H_2O = 3.7 - 4.7$ ), and, as crystallisation from water led to no result, were separated by adding alcohol to the concentrated aqueous solution until no further precipitate was produced. The precipitate (26 grams from 50) consisted of a mixture of the 2:6- and 3:5-salts in the proportion of rather more than three to one, whilst the mother liquor contained only monosulphonate, which crystallised from water in anhydrous needles and was identified both by the chloride and anilide as the 1:4:2-derivative. The mother liquors from which these various separations of hydrated scales had been isolated gave small amounts of the 3:5-disulphonate, and were eventually united with that obtained from the mother liquor of the barium salt, and, as mixtures of mono- and di-sulphonate crystallised in scales on concentration ( $K = 18.54$ ;  $H_2O = 2.78$ ), precipitation with alcohol was resorted to, which effected a separation into 9 grams of mixed 2:6- and 3:5-disulphonate, 8 grams of monosulphonate crystallising from water in anhydrous needles (identified as the 1:4:2-salt) and 10 grams

of monosulphonate left as a residue on evaporation of the alcoholic mother liquor. This residue of monosulphonate, when crystallised from water, separated in monhydrated scales ( $H_2O = 6.38-7.42$ ), and was at first thought to be the 1:4:3-salt, but as the melting point of its chloride could not be raised above  $23^\circ$ , and as the anilides prepared from the crystalline chloride (1.5 grams) and the oily mother liquor (5 grams) melted at  $144-145^\circ$  and  $142-143^\circ$  respectively, it must be regarded as the 1:4:2-derivative, although this salt has not been obtained in a hydrated form from any other source. It follows, therefore, that the whole of the 1:4:3-constituent in the mixed parachlorotoluenesulphonates must have been converted into disulphonic acid on sulphonation under the conditions employed.

As the result of fractional crystallisation, the following quantities of potassium salts, dried at  $160^\circ$ , were accounted for.

	Isolated as salt.	Calculated from chlorides.*	Total.
Parachlorotoluene-2:6-disulphonate...	105	24	129
„ -2:5-disulphonate...	46	7	53
„ -3:5-disulphonate...	24	2	26
„ -sulphone-sulphonate	3	—	3
„ -monosulphonate ...	26	16	42

Deducting the sulphone and the recovered monosulphonate, it follows that the weight of disulphonate accounted for was 208 grams instead of the theoretical yield of 220 grams.

The relative proportions of the 1:4:2- and 1:4:3-isomerides in the mixed parachlorotoluenesulphonic acids may be calculated from these results, because the 2:6-disulphonate has been shown to be produced only from the 1:4:2-salt, and the 3:5-disulphonate only from the 1:4:3-salt, whilst the 2:5-disulphonate is formed from both, and in the approximate proportions of one-third of the former and one-half of the latter. Consequently,

43 grams of 2:5-salt should be formed with 129 grams of 2:6-salt = 172.  
 13 „ „ „ „ 26 „ 3:5-salt = 39.

Hence from the amounts of the 2:6- and 3:5-disulphonates obtained, 56 grams of the 2:5-disulphonate might have been expected instead of the 53 grams actually isolated—a result which may be regarded as indicating substantial agreement. The 220 grams which theoretically should have been obtained would consist therefore of about 40 grams of disulphonate derived from about 27 grams of the 1:4:3-salt, and about 180 grams from about 122 grams of the 1:4:2-salt. Adding to the latter the 42 grams recovered, it follows that the parachloro-

\* See footnote, p. 767.

toluenesulphonates were present in the mixture in the proportion of 27 grams of the 1 : 4 : 3- to 166 grams of the 1 : 4 : 2-salt, or approximately one to six. Parachlorotoluene, therefore, does not yield more than 14 per cent. of the 1 : 4 : 3-isomeride when converted into monosulphonic acids under the conditions described.

*Sulphonation of Potassium Orthochlorotoluene-4-sulphonate.*

Preliminary experiments showed that 20 per cent. anhydrosulphuric acid did not effect sulphonation, so 100 grams of dry potassium orthochlorotoluene-4-sulphonate were heated with 140 grams of 35 per cent. anhydrosulphuric acid at  $150^{\circ}$  during 2 hours, and the product converted into barium salt in the manner already described. The filtrate and washings could not be evaporated conveniently in a dish, as a sparingly soluble barium salt began to separate at once on the surface of the hot liquid, and soon caused bumping, so the concentration was effected in flasks, and continued until crystals appeared, the operation being repeated until 17 grams of sparingly soluble salt had been accumulated, and the solution reduced to 450 c.c. The subsequent separations were considerable in amount, and consisted of a barium potassium salt in very small needles forming a white semi-solid mass, which could be freed easily from any sparingly soluble barium salt by dissolving it in warm water.

The sparingly soluble barium salt, with  $2\text{H}_2\text{O}$ , proved to be the orthochlorotoluene-4 : 5-disulphonate, and was identified by conversion into the potassium salt, with  $1\text{H}_2\text{O}$ , the chloride melting at  $158^{\circ}$ , and the anilide melting at  $183^{\circ}$ . The yield of this isomeride, taking into account the quantity (equivalent to about 3 grams of the barium salt) obtained as potassium salt by extracting the barium sulphate residues with potassium carbonate, amounted to about one-ninth of that theoretically possible.

*Orthochlorotoluene-4 : 6-disulphonic acid.*—The salts of this acid were obtained from the easily soluble barium potassium salt.

The *barium* salt,  $\text{C}_6\text{H}_2\text{MeCl}(\text{SO}_3)_2\text{Ba} + 6\text{H}_2\text{O}$ , obtained from the chloride by hydrolysis with baryta, crystallised in microscopic prisms, and was very soluble in water.

0.4726 lost 0.096  $\text{H}_2\text{O}$  at  $220^{\circ}$ .  $\text{H}_2\text{O} = 20.31$ , theory = 20.40.

0.3766 dry salt gave 0.2044  $\text{BaSO}_4$ .  $\text{Ba} = 31.91$ , theory = 32.50.

The *barium potassium* salt,  $[\text{C}_6\text{H}_2\text{MeCl}(\text{SO}_3)_2]_2\text{BaK}_2 + 3\text{H}_2\text{O}$ , crystallised from water in white masses of very small and easily soluble needles.

0.451 gave 0.0316  $\text{H}_2\text{O}$  at  $235^{\circ}$ .  $\text{H}_2\text{O} = 7.01$ , theory = 6.44.

0.4194 dry salt gave 0.2156 sulphate.  $\text{BaK}_2 = 27.16$ , theory = 27.42.

The *potassium* salt,  $C_6H_2MeCl(SO_3K)_2 + 2H_2O$ , was very soluble in water, and crystallised in large, transparent prisms.

0.455 gave 0.0414  $H_2O$  at  $180^\circ$ .  $H_2O = 9.08$ , theory = 9.04.

0.4136 dry salt gave 0.1986  $K_2SO_4$ .  $K = 21.52$ , theory = 21.52.

The *chloride*,  $C_6H_2MeCl(SO_2Cl)_2$ , crystallised from a mixture of benzene and light petroleum either in octahedral prisms or in aggregates of four-sided plates, dissolved easily in benzene and ether, sparingly in light petroleum, and melted at  $88^\circ$ .

0.1931 gave 0.2571  $AgCl$ .  $Cl = 32.94$ , theory = 32.92.

Mr. W. J. Pope made the following report on the crystals.

"The crystals are large, transparent, orthorhombic octahedra showing the forms  $\{110\}$  and  $\{011\}$ ; they are colourless and transparent, but possess no apparent cleavage.. An optic axis emerges nearly normally through each face of the form  $\{110\}$ . After fusion, the substance solidifies readily in broad, crystalline flakes, most of which are nearly perpendicular to an optic axis; the top face of the flakes is thus evidently  $\{110\}$ ."

The *anilide*,  $C_6H_2MeCl(SO_2NHPh)_2$ , crystallised from dilute alcohol in small, elongated plates, dissolved easily in alcohol, very sparingly in benzene, and melted at  $180^\circ$ .

0.3826 gave 20 c.c. moist nitrogen at  $17.5^\circ$  and 768 mm.

$N = 6.22$ , theory = 6.41.

The constitution of this acid was determined by reducing the potassium salt in aqueous solution with 2 per cent. sodium amalgam, and isolating the product by precipitation with alcohol in the manner already described. The resulting toluenedisulphonate was converted into chloride, which crystallised from petroleum (b. p.  $90-120^\circ$ ) in needles melting at  $56^\circ$ , and was identified as toluene-2:4-disulphonic chloride. The corresponding anilide melted at  $187^\circ$ . The chloro-acid, therefore, must be orthochlorotoluene-4:6-disulphonic acid.

#### *Sulphonation of Potassium Orthochlorotoluene-5-sulphonate.*

After a preliminary experiment, 50 grams of dry potassium orthochlorotoluene-5-sulphonate were heated with 85 grams of 20 per cent. anhydrosulphuric acid at  $150^\circ$  during 2 hours. The product was converted into barium salt, which crystallised slowly from concentrated solutions in tufts of silky needles, seemed to be uniform, and had the composition expressed by the formula  $C_6H_2MeCl(SO_3)_2Ba + 4\frac{1}{2}H_2O$ . The potassium salt, being very soluble in water, was fractionally crystallised from dilute alcohol. Several fractions crystallising in short prism-



atic needles were obtained, which were apparently uniform, although the amount of water of crystallisation was not constant (6·73—8·04 per cent.); the yield amounted to 58 grams of salt dried at 160°. Towards the end of the fractionation, 4 grams of salt was obtained crystallising in thin scales ( $K = 16\cdot85$ ;  $H_2O = 6\cdot89$ ), and was evidently impure monosulphonate, the final mother liquors, on evaporation, giving 6 grams of residual salt which was not examined further.

The potassium disulphonate was recrystallised from water to ascertain whether it separated in two forms like the salt prepared from orthotoluidine-3 : 5-disulphonic acid. This was found to be the case, and, although crystals separated slowly both from concentrated and from more dilute solutions, the former were in radiate tufts of very small needles ( $H_2O = 8\cdot91$ ) and the latter in massive prisms ( $H_2O = 11\cdot03$ ). The acicular crystals, when allowed to remain in the mother liquor overnight, usually changed into small, prismatic scales ( $H_2O = 9\cdot80$ ). The salt was evidently potassium orthochlorotoluene-3 : 5-disulphonate, and its identity was placed beyond doubt by examination of the chloride melting at 85°, and the anilide melting at 183°.

Similar results were obtained by sulphonating orthochlorotoluene with 6·5 times its weight of 20 per cent. anhydrosulphuric acid at 150°, and it follows, therefore, that orthochlorotoluene-3 : 5-disulphonic acid is the production of sulphonation in both cases.

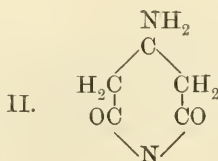
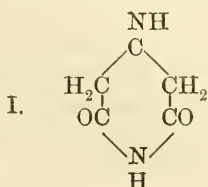
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## LXXXII.—*Chlorine Derivatives of Pyridine. Part II.* *Interaction of Ammonia and Pentachloropyridine.* *Constitution of Glutazine.*

By W. T. SELL, M.A., F.I.C., and F. W. DOOTSON, M.A.

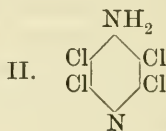
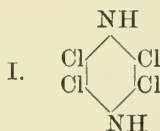
IN a communication "On the Synthesis of Pyridine Derivatives" by Stokes and Pechmann (*Ber.*, 1887, 20, 2655, and *Amer. Chem. J.*, 1886, 6, 377), it has been shown that, by a series of reactions, ethylic acetone-dicarboxylate may be converted into glutazine which is undoubtedly a pyridine derivative.

The constitution of this substance is left open as between the following alternative formulæ,





Subsequent work on this important substance has not sufficed to prove which of the two is correct. Among other reactions which Stokes and Pechmann tried with a view to obtain evidence of the constitution of glutazine, that of a solution of phosphorus pentachloride in phosphorus oxychloride was examined; this gave rise to various chlorinated products of which we are mainly concerned with but one, namely, amidotetrachloropyridine, to which the alternative formulæ

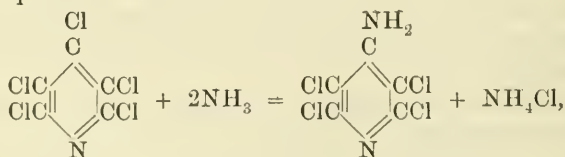


were assigned (*loc. cit.*).

From a consideration of the properties of this and other derivatives, Stokes and Pechmann expressed a preference for the constitution represented by formula II.

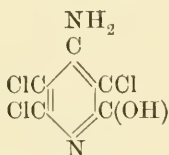
As will be seen below, by the action of ammonia on pentachloropyridine several compounds have been isolated, but of the three possible derivatives in which one atom of chlorine is replaced by amidogen, two only have been obtained, the third, if formed at all, being too small in quantity to be detected. One of these isomeric amidotetrachloropyridines, which does not require a temperature higher than  $100^{\circ}$  for its formation, corresponds in fusing point, crystalline form, solubility, and general properties with the similar compound described by Stokes and Pechmann, and is obviously identical with it, this identity being confirmed by the action of sodium ethoxide on the compound, by which a second chlorine atom is replaced, and amidoethoxytrichloropyridine formed. This product also agrees with the corresponding substance described by Stokes and Pechmann, in fusing point, crystalline form, and general behaviour.

Since, from the method of preparation, the reaction between pentachloropyridine and ammonia without doubt takes place in accordance with the equation



our experiments must be regarded as a confirmation of the existence of the amido-group in the chlorinated product of glutazine, and therefore in glutazine itself, since, at the temperature at which these reactions were carried out, there is no reason to suppose a transference of the hydrogen atom to have taken place.

Although the generally reactive nature of the  $\alpha$ -position renders it extremely probable that in the second amidotetrachloropyridine obtained, the amido-group occupies the ortho-position relatively to the nitrogen, we have, so far, not succeeded in obtaining experimental evidence of this. An attempt was, however, made as follows. The amido-group was replaced by hydroxyl by a modification of Bouveault's method (*Bull. Soc. Chim.*, 1892, [iii], 9, 368), and the hydroxytetrachloropyridine thus formed was treated with ammonia. By these means, it was expected that the compound shown by Stokes and Pechmann to have the structural formula



would be obtained, from the known ease with which the para-position is attacked by ammonia. The product of the reaction, however, although closely resembling this substance in properties and appearance, was not identical with it. In view of the fact that there are four theoretically possible monamido-derivatives of  $\alpha$ -hydroxytetrachloropyridine, this experiment must be regarded as inconclusive. Want of material prevented us from pursuing the investigation at this stage.

An attempt to demonstrate that the amido-group was in the  $\alpha$ -position, by converting amidoethoxytrichloropyridine into diamidopyridine also failed, the ethoxy-group being quite stable at temperatures at which the remaining chlorine is attacked by ammonia.

Of the six theoretically possible diamido-derivatives of pentachloropyridine, only one has been isolated. This compound is obtained by the further action of ammonia on either of the amidotetrachloropyridines mentioned above.

#### EXPERIMENTAL.

Pentachloropyridine is not acted on in the cold by aqueous or alcoholic ammonia of any strength. At a temperature approaching  $100^\circ$ , however, one atom of chlorine is attacked, whilst between  $150^\circ$  and  $180^\circ$  a second atom is replaced by amidogen.

Numerous experiments were carried out at temperatures varying between  $100^\circ$  and  $150^\circ$ , with the object of determining the conditions under which each monamido-derivative is formed in largest amount, and of obtaining the third theoretically possible tetrachloramidopyridine; in the latter, however, as stated above, we were not

successful. It was not found that the yield of each of the others varied materially under the conditions tried; that of  $\gamma$ -amidotetrachloropyridine was always somewhat in excess of the other at temperatures below  $150^{\circ}$ , whilst above  $150^{\circ}$  the former is converted into diamidotrichloropyridine more readily than the latter compound.

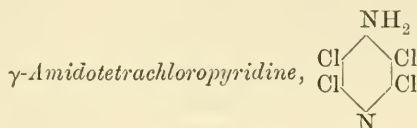
For the purpose of these experiments, pentachloropyridine, prepared by the action of phosphorus pentachloride on dry pyridine as described by the authors (*Trans.*, 1898, **73**, 433), was heated at  $100$ — $110^{\circ}$  for about 4 hours with alcoholic ammonia in sealed tubes, and the contents of the tubes thrown on to a filter, and washed with cold alcohol or ether by the aid of the pump. In the earlier experiments, when the temperature had been allowed to approach  $150^{\circ}$ , the residue left on the filter-plate was then washed repeatedly with cold, moderately dilute hydrochloric acid, to dissolve any diamidotrichloropyridine present, but when the heating had been carried on at  $100^{\circ}$  to  $120^{\circ}$ , this precaution was unnecessary. After 4 hours heating at  $100^{\circ}$ , the amount of pentachloropyridine remaining unacted on is negligible, but if necessary it can be removed by distilling the product in a current of steam, in which the amidotetrachloropyridines are only very slowly volatile. After one recrystallisation from alcohol, the  $\gamma$ -amidotetrachloropyridine thus obtained is practically pure.

The alcoholic filtrate mentioned above, on evaporation, deposits long silky needles of the second product, which, however, can only be freed from the last traces of the  $\gamma$ -amido-derivative by many recrystallisations from alcohol, or, more readily, by frequent washing on the filter-plate with small quantities of ether, when the greater part of the latter product is left behind.

As stated above, the diamido-derivative is obtained by heating pentachloropyridine or either of its monamido-derivatives for several hours at  $170$ — $180^{\circ}$ , preferably with equal parts of alcoholic and strong aqueous ammonia, evaporating the alcohol and excess of ammonia, and dissolving the residue in moderately dilute hydrochloric acid. After filtration, the diamidotrichloropyridine is reprecipitated by alkali, and purified by recrystallisation from water or 50 per cent. alcohol.

It is interesting to note that, although the  $\gamma$ -amido-group is somewhat more easily introduced than the other one, as shown by the greater yield of  $\gamma$ -amidotetrachloropyridine at low temperatures, yet the latter compound is the more easily attacked as the temperature is raised. This was shown by parallel experiments in which equal weights of the two substances were heated at  $170$ — $180^{\circ}$  for 4 hours, with alcoholic ammonia alone, in the same oven. On opening the tubes, it was found that about half of the  $\gamma$ -amidotetrachloropyridine was converted into diamidotrichloropyridine, whereas the remaining

tube gave the merest trace of diamido-derivative. When equal parts of alcoholic and strong aqueous ammonia were used, the conversion, in both cases, was practically complete.



This compound, obtained by the methods described above, crystallises from alcohol in thin, colourless scales, or, particularly when deposited slowly, in cubes or modifications of cubes. These crystals, which melt at 212—213° (uncorr.), gave the following numbers on analysis.

0.1160 required 20.0 c.c. N/10 AgNO<sub>3</sub>. Cl = 61.03 (Trans., 1898, 437).

0.2630 gave 27.5 c.c. nitrogen at 12° and 748 mm. N = 12.15.

C<sub>5</sub>N<sub>2</sub>Cl<sub>4</sub>H<sub>2</sub> requires Cl = 61.14; N = 12.06 per cent.

This substance is fairly soluble in ether, benzene, and hot alcohol, slightly in cold alcohol, but practically insoluble in water, dilute acids, and alkalis. Strong sulphuric acid dissolves it readily in the cold. It shows no basic properties, and does not form a platinumchloride. When boiled for 2 hours with excess of a solution of sodium ethoxide in absolute alcohol, it yields  $\alpha$ -ethoxy- $\gamma$ -amidotrichloropyridine, melting at 83° (uncorr.) (*Amer. Chem. J.*, 1886, 6, 393).

*Amidotetrachloropyridine melting at 174—175° (uncorr.).*—This crystallises in long, silky needles, readily soluble in hot alcohol, ether, benzene and chloroform, and fairly in cold alcohol. Water and dilute mineral acids dissolve it to a slight extent on boiling, and from these it crystallises in tufts of fine, colourless needles. Strong sulphuric acid dissolves it readily in the cold. It is not acted on by boiling alkalis, and is only very slowly volatile in steam. A specimen recrystallised from alcohol and melting at 174—175° gave the following numbers on analysis.

0.1750 gave 0.4332 AgCl. Cl = 61.24.

0.1850 „ 19.0 c.c. nitrogen at 18° and 758 mm. N = 12.03.

C<sub>5</sub>N<sub>2</sub>Cl<sub>4</sub>H<sub>2</sub> requires Cl = 61.14; N = 12.06 per cent.

*Hydroxytetrachloropyridine* was obtained from the amidotetrachloropyridine melting at 174—175°, described above, by a modification of Bouveault's method (*loc. cit.*); the latter consists in dissolving the substance in strong sulphuric acid and cautiously adding the theoretical amount of concentrated sodium nitrite solution, the temperature meanwhile being kept at 30—40°, finally heating for a few minutes to 40—50°. The modification lay in dissolving the substance in



the least possible quantity of strong sulphuric acid, and adding excess of sulphuric acid previously charged with nitrous fumes. After heating on the water bath for 20 minutes and cooling somewhat, water was cautiously added in very small quantities with frequent agitation. When the evolution of gas slackened, the flask was again heated on the water bath for half an hour, and the contents finally poured into water. The copious precipitate thus obtained was collected, washed, and digested with a warm dilute solution of sodium carbonate, in which the hydroxytetrachloropyridine is readily soluble, and therefore easily separated by filtration from any unchanged amidotetrachloropyridine. On neutralising the filtered solution with acetic acid, the substance was again precipitated, and was purified by recrystallisation from dilute alcohol.

Hydroxytetrachloropyridine thus prepared melted at 220—221°, and gave the following numbers.

0.1273 gave 6.8 c.c. nitrogen at 22° and 762 mm.  $N = 6.07$ .

0.1210 „ 6.5 c.c. „ at 20° „ 762 mm.  $N = 6.13$ .

$C_5NCl_4 \cdot OH$  requires  $N = 6.02$  per cent.

This compound is readily soluble in ether and alcohol, both hot and cold, moderately so in benzene, from which it crystallises in aggregates of colourless needles, slightly in concentrated hydrochloric acid, and readily in strong sulphuric acid, but is practically insoluble in water. Dilute alkalis and alkali carbonates dissolve it readily on warming. A solution of the ammonium salt may be evaporated to dryness without decomposition. With *barium chloride*, the ammonium salt gave a white precipitate of colourless needles, at once in a strong solution, but if dilute, only on standing; this precipitate was not redissolved on boiling. With *silver nitrate*, a gelatinous white precipitate is formed, insoluble in boiling water. With *ferric chloride*, hydroxytetrachloropyridine gives a red coloration only on boiling. After heating for 5 hours to a temperature of 130° with strong aqueous ammonia, the substance was found to be unchanged.

*Diamidotrichloropyridine* was obtained as described above from pentachloropyridine or from amidotetrachloropyridine; purified by recrystallisation from dilute alcohol, it melts at 206° to 207°.

0.1250 gave 0.2527 grams  $AgCl$ .  $Cl = 50.05$ .

0.1488 „ 26.1 c.c. nitrogen at 22° and 760 mm.  $N = 19.85$ .

$C_5N_3Cl_3H_4$  requires  $Cl = 50.04$ ;  $N = 19.79$  per cent.

This compound is readily soluble in alcohol, from which it separates in pearly scales of rather indefinite outline, or in needles pointed at the ends; it is fairly soluble in ether, acetone, and hot benzene, crystallising from the latter in large, flat needles; moderately soluble



in hot water, but practically insoluble in the cold. Dilute acids dissolve it easily, and from these it is reprecipitated by alkalis. On adding platinic chloride to its solution in alcohol or dilute hydrochloric acid, the platinumchloride separates in short, thick needles, at once if the solution is concentrated, but only on standing when dilute; it is very sparingly soluble in hot water. The air-dried crystals lost, at  $120^{\circ}$ , an amount which approximately corresponds with  $3\text{H}_2\text{O}$ , whilst the dry salt gave the following numbers.

0.2864 gave 0.0674 Pt. Pt = 23.53.

$(\text{C}_5\text{N}_3\text{Cl}_3\text{H}_4)_2, \text{H}_2\text{PtCl}_6$  requires Pt = 23.37 per cent.

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### LXXXIII.—*Mercury Acetamide.*

By MARTIN ONSLOW FORSTER, Ph.D., B.Sc.

It has long been known that yellow mercuric oxide is dissolved readily by an aqueous solution of acetamide, and that the liquid deposits a colourless, crystalline compound on evaporation; this observation was made by Strecker (*Annalen*, 1857, 103, 324). Since the time of its discovery, mercury acetamide has received attention from Tafel and Enoch (*Ber.*, 1891, 23, 1553), and from Seliwanoff (*Ber.*, 1893, 26, 423 and 987), but it was not made the subject of special study by these investigators, whose references to it are merely incidental.

Having noticed that the substance acts with vigour on phenylhydrazine, I was led to examine the products of the change, and, finding the subject one of some interest, extended the investigation to other typical derivatives of nitrogen. The present paper contains an account of the experiments made in this connection.

#### *Action of Mercury Acetamide on Hydroxylamine.*

The interaction of mercury acetamide and hydroxylamine is somewhat complicated. It proceeds in different directions according as the free base or the hydrochloride is under examination; moreover, the action of the metallic compound is materially modified in the case of the salt by treating the latter with the former, instead of *vice versa*.

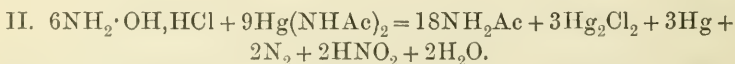
When mercury acetamide dissolved in water is slowly added to an aqueous solution of hydroxylamine hydrochloride, already made alka-

line with potassium carbonate, vigorous effervescence takes place. The first drop of the liquid produces a transient, bright yellow precipitate, the colour of which changes instantly to the dark grey of finely-divided mercury; as more of the solution is added, heat is developed, and the spongy precipitate of mercury increases largely in bulk, until a stage is reached at which no effervescence is perceptible on adding another drop of the solution. If this experiment is carried out with normal solutions, it is found that 5 c.c. of the dissolved hydroxylamine hydrochloride, made alkaline with 10 c.c. (1 mol.) of a normal solution of potassium carbonate, require exactly 4 c.c. of the aqueous mercury acetamide to be added before effervescence ceases and the filtered liquid gives no turbidity with a drop of either solution. Five molecular proportions of the free base are therefore capable of replacing mercury by hydrogen in four of the mercury compound, the action being represented by the equation



The precipitate obtained in the above experiment dissolved completely in warm, dilute nitric acid; whilst the filtrate contained potassium nitrite and acetamide. Two estimations of the quantity of gas liberated from a known weight of hydroxylamine hydrochloride gave results corresponding with 16.34 and 15.74 per cent. respectively; the pure salt contains 20.18 per cent. of nitrogen, and four-fifths of this quantity, the amount required by equation I, is 16.15 per cent.

When hydroxylamine hydrochloride alone is titrated with mercury acetamide, however, two molecular proportions of the hydrochloride completely reduce three of mercury acetamide, a relation which differs widely from that holding good when the free base only is involved. This divergence is due to the fact that chlorine plays a part in the change. The spongy precipitate obtained on mixing the two solutions consists of calomel and mercury, whilst nitrous acid occurs in the filtrate. The interaction of mercury acetamide and hydroxylamine hydrochloride, when the former is added to the latter, may be expressed as follows.



According to this equation, hydroxylamine hydrochloride should yield 13.46 per cent. of gaseous nitrogen, instead of 16.15 per cent. obtained by decomposing the free base. On passing rather more than the necessary amount of mercury acetamide solution into a tube containing hydroxylamine hydrochloride over mercury, quantities representing 14.34 per cent, and 14.23 per cent. were obtained.

Although equation II most probably represents the final result of the action, indications are not wanting to show that intermediate products are formed. The first few drops of the mercury derivative produce scarcely any effervescence in the liquid ; the formation of a greenish-yellow precipitate, instantly changing to dirty white, is the initial result of action, and, although bubbles of gas continue to rise during the addition of the first portions of the metallic derivative, effervescence does not become general and vigorous until quite one-third has been used. In the light of experiments to be subsequently described, these circumstances point to the formation of an unstable, additive compound of mercury acetamide with hydroxylamine hydrochloride, undergoing decomposition as more of the former is added.

A third set of conditions prevails when mercury acetamide is treated with hydroxylamine hydrochloride ; in this case, the latter is capable of reducing two molecular proportions of mercury acetamide. Although this relation is apparently very simple, complications are introduced by the formation of one or more intermediate compounds, as indicated by the following facts.

When aqueous hydroxylamine hydrochloride is delivered drop by drop into a dilute solution of mercury acetamide while the latter is constantly agitated, a bright yellow precipitate is first formed, and rapidly changes<sub>es</sub> to dark greenish-brown, but a considerable proportion of the total quantity of salt must be added before effervescence becomes perceptible. If the precipitate formed by the first few drops is collected and washed with water, it effervesces vigorously when treated with hydroxylamine hydrochloride, showing that, in presence of excess of mercury acetamide, an intermediate compound is formed, capable of giving up its nitrogen when brought in contact with hydroxylamine hydrochloride. By removing the precipitate formed with every few drops of the hydrochloride, before the next addition is made, it is possible to remove nearly all the available nitrogen in this form, scarcely any effervescence being noticeable under these conditions. In consequence of the complicated influences bearing on this change, the volume of nitrogen obtained on treating the mercury solution with hydroxylamine hydrochloride is variable, the latter yielding about 16—18 per cent. of the gas.

Experiments conducted with a solution of hydroxylamine hydrochloride rendered alkaline with potassium carbonate have shown that, on adding this solution to mercury acetamide, the effect of adding the latter to the former is scarcely modified.

It will be seen that, by means of mercury acetamide, hydroxylamine may be estimated with rapidity and accuracy. It is only necessary to render the solution alkaline with potassium carbonate before titrating

with a standard solution of mercury acetamide, which is delivered from a burette in small quantities at a time; when effervescence slackens, the metallic derivative is added more cautiously until no liberation of gas occurs with one drop of the solution. It is generally possible to recognise this stage in spite of the mercury suspended in the liquid, but, in doubtful cases, a few drops of the liquid may be filtered, and tested with a solution of the mercury compound. The method should gain in utility from the fact that neither nitrites nor sulphites have any action on mercury acetamide.

*Action of Mercury Acetamide on  $\beta$ -Phenylhydroxylamine and on the Nitroso-derivative.*

On agitating an ethereal solution of  $\beta$ -phenylhydroxylamine with cold, aqueous mercury acetamide, mercury is at once precipitated, the ether becomes deep green, and acquires the characteristic, pungent odour of nitrosobenzene. If a solution of the mercury derivative is added to water in which phenylhydroxylamine is suspended, the metal is precipitated, and considerable rise of temperature takes place; on heating the liquid, nitrosobenzene condenses on the cool parts of the tube. Preliminary experiments having shown that mercury acetamide is capable of decomposing approximately two molecular proportions of phenylhydroxylamine, the action between these compounds was observed under the following conditions.

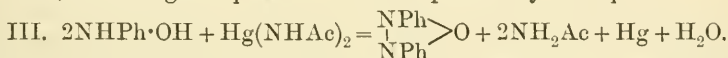
Twenty-two grams of phenylhydroxylamine were suspended in cold water, and treated with 100 c.c. of the normal solution of mercury acetamide, which was added in small quantities at a time to the well-stirred liquid. No liberation of gas occurred as in the case of hydroxylamine, but the liquid soon became warm, and acquired the penetrating odour of nitrosobenzene. A beaker was found the most convenient vessel in which to carry out the operation, because crystals of phenylhydroxylamine become entangled in the heavy, oily product, and these, unless crushed, and brought into contact with the solution, are liable to escape decomposition. When the prescribed quantity of mercury acetamide had been added, a portion of the liquid was boiled and filtered, the pale yellow solution no longer giving a precipitate with either phenylhydroxylamine or mercury acetamide. A current of steam was, therefore, passed through the whole product; the first portion of the distillate consisted of nitrosobenzene, obtained as a dark green oil, which rapidly crystallised in colourless, transparent plates melting at 67—68°; the quantity did not exceed 0.25 gram.

On continuing the distillation, a pale yellow oil passed over very slowly, about one gram being obtained in 1—2 hours; the operation

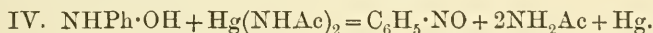


was therefore interrupted, and the distillate and residue extracted separately with ether, which in each case deposited a yellow oil when dried and evaporated. The product quickly solidified in long needles melting at  $36^{\circ}$ , and was identified with azoxybenzene; it weighed 16 grams. The residual liquid in the distilling flask, after extraction with ether, was filtered from mercury, and evaporated on the water bath until the odourless liquid was anhydrous. The viscous fluid rapidly solidified when cold, and in this manner 10 grams of acetamide were recovered.

It being clear that mercury, azoxybenzene, and acetamide are the main products of the action of mercury acetamide on phenylhydroxylamine, the change in question is well expressed by the equation



In order to account for the production of nitrosobenzene, it is necessary to suppose that a small quantity of phenylhydroxylamine acts with one molecular proportion of mercury acetamide instead of with two, and simply parts with two atoms of hydrogen: thus



In these circumstances, it was to be expected that the yield of nitrosobenzene might be augmented if, instead of adding the mercury compound to phenylhydroxylamine, the converse order of treatment was observed. Nine grams of phenylhydroxylamine were therefore added in small quantities to 50 c.c. of normal mercury acetamide solution at  $40$ – $50^{\circ}$ . On passing steam through the product, it was found that another gram of phenylhydroxylamine was sufficient to remove all the mercury from solution. The proportion of hydroxylamine derivative to mercury acetamide was therefore lower than in the first case, as equation IV requires; the nitrosobenzene which distilled over weighed 0.75 gram, representing a yield just six times more favourable than that obtained under the conditions of the previous experiment.

From these results, it is evident that mercury acetamide derives the hydrogen required to liberate the metal almost exclusively from the imino-group of the hydroxylamine derivative. It became of interest, therefore, to examine the behaviour towards the former compound of a substance in which the iminic hydrogen is replaced. The nitroso-derivative is the most convenient for this purpose, and, as might be expected, no precipitation of mercury occurs on treating the alcoholic solution with mercury acetamide. On the contrary, combination takes place between molecular proportions of the two substances, yielding a definite, crystalline, double compound.



Six grams of nitroso- $\beta$ -phenylhydroxylamine were dissolved in alcohol, and treated with a solution of 13.7 grams (1 mol.) of mercury acetamide in 75 per cent. alcohol, and the bulky, greenish-yellow precipitate which immediately separated was collected and washed with alcohol. After being drained on porous earthenware, it was crystallised from boiling acetone, in which it dissolves somewhat freely, separating in pale yellow, lustrous needles as the liquid cools. It gives Liebermann's reaction, and melts to a deep brown liquid at  $125^{\circ}$ , when gas is liberated.

0.2346 gave 24.5 c.c. of moist nitrogen at  $24^{\circ}$  and 764 mm.  $N = 11.77$ .

$C_6H_6N_2O_2, Hg(NHAc)_2$  requires  $N = 12.33$  per cent.

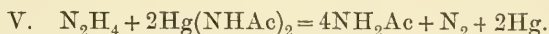
The substance is quite insoluble in boiling water, but dissolves readily in hot alcohol, from which it separates in pale yellow needles mingled with amorphous nodules; acetone is, therefore, a more convenient solvent to employ for recrystallisation, but the solution in this medium, which is pale yellow at first, becomes green after some hours, or more quickly when boiled. Caustic soda decomposes it, changing the colour of the crystals to brown; the filtrate, however, gives no precipitate when acidified. Dilute hydrochloric acid, on the other hand, dissolves the substance when gently heated, caustic soda giving a yellow precipitate in the liquid; on boiling the solution, nitrosobenzene is produced. Cold, concentrated sulphuric acid decomposes the double compound, and develops a deep green coloration.

#### *Action of Mercury Acetamide on Hydrazine.*

In many respects, the behaviour of hydrazine towards mercury acetamide recalls that of hydroxylamine. Both substances readily replace mercury by hydrogen in the metallic derivative, converting it into mercury and acetamide, while nitrogen is set free. Moreover, in the case of each base, the action differs from that occurring with the hydrochloride, the latter giving rise to mercurous chloride. A third point of resemblance lies in the fact that hydrazine hydrochloride is capable of precipitating a larger proportion of mercury acetamide when it is added to the latter than when it is treated with it. There is, however, one most important difference. Whilst only four-fifths of the nitrogen in hydroxylamine, and two-thirds of that in the hydrochloride, are liberated by the agency of mercury acetamide, this compound sets free all the nitrogen from both hydrazine and its hydrochloride.

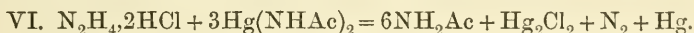
A standard solution of hydrazine hydrochloride was prepared containing 1 gram molecule in 4,000 c.c. of the liquid. Four c.c. were

then treated with an equal bulk of normal potassium carbonate, and titrated with normal mercury acetamide. The first drop produced a bright yellowish-green precipitate, which instantly became dark grey; as more of the metallic solution was added, effervescence took place and heat was developed. The above quantity of hydrazine solution required 2.05 c.c. of normal mercury acetamide for complete oxidation, and in a second experiment 3.05 c.c. were required by 6 c.c. of the base. Under these conditions, therefore, hydrazine is capable of reducing two molecular proportions of mercury acetamide, as represented by the equation



The volume of gas actually liberated agrees with the quantity required by this expression. In two experiments, 4 c.c. of the hydrazine solution yielded quantities of nitrogen representing 27.66 per cent. and 26.55 per cent. of the salt employed; hydrazine hydrochloride contains 26.74 per cent. of nitrogen.

The hydrochloride alone was next titrated with mercury acetamide, when the salt was found capable of precipitating mercury from three molecular proportions of mercury acetamide, according to the equation



As in the corresponding case of hydroxylamine hydrochloride, the precipitate was a mixture of mercury and calomel.

In adding the solution of mercury acetamide, it was noticed that the first drop produced a yellow precipitate which rapidly darkened without liberating gas; further quantities changed the colour of the suspended matter to dirty white, still without any considerable evolution of gas, until, when more than half the necessary quantity had been added, the precipitate became dark grey, and brisk effervescence took place. These changes were more noticeable in the following experiment. Four c.c. of normal mercury acetamide were added in four equal portions to the same volume of hydrazine hydrochloride contained in a graduated tube over mercury. The first addition precipitated a dirty white solid in the liquid, and produced about 2 c.c. of gas, approximately twice this quantity arising from the second c.c. of the mercury solution, which also increased the bulk of the white precipitate; the latter became grey when the third portion was added, about 15 c.c. of nitrogen being generated; and the fourth c.c., without altering the appearance of the solid product, slightly increased the volume of gas. In all, 24.6 c.c. of moist nitrogen at 20.5° and 768 mm. were obtained, representing 27.10 per cent. of nitrogen in the hydrochloride employed. This result agrees with the requirements of

equation VI, from which hydrazine hydrochloride is expected to yield the total theoretical amount (26·74 per cent.) of nitrogen.

If, instead of adding mercury acetamide to hydrazine hydrochloride, the former is titrated with the latter, the mercury derivative is capable of decomposing only a quarter molecular proportion of the salt. Although the relation between the two substances is, under these conditions, a simple one, it will be found difficult to express the course of the change by an equation. There can be no doubt that the reaction is complicated by the formation of intermediate products, as in the case of hydroxylamine hydrochloride. It is quite possible that the high proportion of mercury acetamide required to satisfy the hydrochlorides in question, when the latter are added to it, is due to combination occurring between the unaltered substance—which is in local excess—and the mercurous chloride generated in the action. Although this view gains support from the fact that mercury acetamide forms an insoluble compound with mercurous nitrate, it must be admitted that the precipitate formed on adding hydrazine hydrochloride to mercury acetamide does not yield ammonia when boiled with soda; if it contained a compound of the nature indicated above, one would expect ammonia to be produced.

*Action of Mercury Acetamide on Phenylhydrazine and its Derivatives.*

When dry mercury acetamide is added to phenylhydrazine, mercury is at once precipitated in a finely divided state. Separation of the metal is attended with rapid and considerable rise of temperature, whilst a relatively large volume of gas is liberated; at a very short interval, the odour of benzene becomes perceptible. If the action is moderated by the presence of water, it becomes possible to follow its course, and isolate the products.

Fifty grams of phenylhydrazine were suspended in about 100 c.c. of water, and treated with an aqueous solution of 73 grams ( $\frac{1}{2}$  mol.) of mercury acetamide. The latter was added in small quantities at a time, each addition giving rise to vigorous effervescence, accompanied by considerable rise of temperature, whilst finely divided mercury was precipitated, and quickly collected in a shining globule. After the prescribed amount of mercury acetamide had been added, it was found necessary to treat the liquid with about 10 grams more before gas ceased to be evolved. A pronounced odour of benzene had meanwhile become perceptible, and the flask was, therefore, connected with a condenser, and heated on a water bath. The distillate, when washed with dilute hydrochloric acid, and dried with calcium chloride, passed over entirely below 80°, and was readily identified with the hydrocarbon: it weighed 10 grams.

After the greater part of the benzene had been removed, a current

of steam was passed through the liquid, and when the distillate, which was at first pale yellow, no longer floated on water, the receiver was changed, and the distillation continued until all volatile matter excepting mercury had been removed. Neither the heavy, red oil obtained in this way, nor the yellow product forming the first fraction, was capable of reducing Fehling's solution, showing that the phenylhydrazine employed in the experiment had been completely decomposed. In order to remove non-basic substances, the combined distillate was treated with hydrochloric acid and distilled in a current of steam; alkali was then added, and steam again passed through the liquid, which yielded 15 grams of aniline boiling at  $181^{\circ}$ .

The mercury remaining in the distilling flask weighed 50 grams. A small quantity of a dark-brown oil, which had resisted the continued action of steam, solidified as the liquid cooled, and when spread on porous earthenware yielded pale brown crystals which became almost colourless when washed with cold alcohol. The substance contained mercury, and crystallised from boiling alcohol in lustrous, pale-yellow needles melting at  $125\text{--}126^{\circ}$ ; scarcely soluble in cold alcohol, it dissolved freely in benzene, however, and therefore agreed closely with the described properties of mercury diphenyl.

Benzene, aniline, mercury, and mercury diphenyl having been thus removed, the dark-brown liquid, which had a powerful, tarry odour, was boiled with animal charcoal, filtered, and evaporated; the residue remained liquid when all the water had been removed, but rapidly crystallised when the source of heat was withdrawn. The product, consisting of acetamide, weighed 14.5 grams, and did not yield ammonia when treated with cold, aqueous soda.

It is noteworthy that acetamide recovered from the mercury derivative by the action of such reducing agents as hydroxylamine, phenylhydroxylamine, and phenylhydrazine, is absolutely odourless; when distilled, however, it acquires the characteristic odour associated with acetamide prepared by ordinary methods.

The amount of mercury recovered from the liquid being almost equal to that required by theory (50 grams instead of 53) suggested the possibility of estimating the quantity of phenylhydrazine in a commercial specimen of the base, by weighing the metal set free from a slight excess of mercury acetamide. Experiments were, therefore, undertaken, with a view to ascertain whether concordant determinations could be made in this way. A known weight of phenylhydrazine was treated in a small weighed beaker with finely powdered mercury acetamide, which, in small quantities at a time, was added until bubbles of gas no longer appeared; after an interval, the globule of mercury was washed by decantation several times with alcohol, dried in the desiccator, and weighed.



I.	1.7253	phenylhydrazine	gave	1.6909 Hg.	Hg = 98.0 per cent.
II.	1.0978	"	"	1.0679 Hg.	Hg = 97.3 "
III.	1.2217	"	"	1.1788 Hg.	Hg = 96.5 "
IV.	1.1313	"	"	1.1172 Hg.	Hg = 98.7 "

The proportion of metal to be expected on adding exactly a half molecular proportion of mercury acetamide is 92.6 per cent. of the weight of phenylhydrazine employed; as might have been anticipated from the result of the experiment conducted on a large scale, somewhat more than this quantity is precipitated in the ultimate decomposition of the base. The determinations quoted, however, are in sufficient agreement with one another to show that mercury acetamide will afford a means of estimating phenylhydrazine when a standard percentage of metal corresponding to the pure base has been established.

A curious feature of the precipitation of mercury with phenylhydrazine is worthy of note. When finely divided mercury acetamide is added to the base, mercury separates as a grey powder, and after a few minutes aggregates to a lustrous globule which may be easily washed by decantation without loss. If, on the other hand, the mercury compound is covered with excess of phenylhydrazine, the metal remains in the form of powder even after continued treatment with alcohol; the mercury, however, if washed carefully, may be weighed without serious loss, as the following determinations will show.

I.	1.3014	mercury acetamide	gave	0.7891 Hg.	Hg = 60.6 per cent.
II.	0.9773	"	"	0.5988 Hg.	Hg = 61.3 "
III.	1.2213	"	"	0.7517 Hg.	Hg = 61.5 "
IV.	1.1490	"	"	0.7115 Hg.	Hg = 61.9 "

$\text{Hg}(\text{NHAc})_2$  requires Hg = 63.3 per cent.

The action of mercury acetamide on phenylhydrazine cannot be represented by a simple equation. It is possible to formulate the change by an expression based on the yield of benzene and aniline obtained experimentally, and on the relative quantities of the mercury compound and phenylhydrazine required for complete mutual decomposition, but such an equation would take no account of the production of mercury diphenyl; moreover, the quantity of gas actually evolved falls considerably below the expected amount, probably owing to the formation of resinous products rich in nitrogen. It is not unlikely that phenyldiazoimide is also produced, although this substance was not isolated: it is formed in small quantities when mercuric oxide is treated with a solution of phenylhydrazine sulphate, diazobenzene sulphate being the chief product. Mercuric oxide converts



the free base into aniline, nitrogen, and mercury diphenyl (E. Fischer, *Annalen*, 1879, 199, 320).

The activity which phenylhydrazine displays towards mercury acetamide is reflected by its derivatives. When, for instance, the mercury compound, dissolved in water, is added drop by drop to aqueous phenylhydrazine hydrochloride, a dirty white precipitate is formed, and becomes dark olive green with more of the agent, which induces slow and continuous effervescence; the precipitate, when filtered and washed, yields mercurous chloride on treatment with hot, dilute nitric acid. An alcoholic solution of acetylphenylhydrazine, treated with mercury acetamide dissolved in 75 per cent. alcohol, remains clear for a few seconds, when finely divided mercury suddenly appears; more vigorous action takes place on heating the liquid, which ultimately yields a heavy precipitate of the metal. Pyruvic phenylhydrazone, phenylglucosazone, and phenylsemicarbazide resist the action of mercury acetamide in cold solutions, but undergo oxidation when heated with it, mercury being precipitated. Benzylidene-phenylhydrazone may be boiled during 1—2 minutes with alcoholic mercury acetamide without undergoing appreciable change; on allowing the liquid to stand, however, it becomes cherry-red, finally acquiring a deep, port-wine colour, and mercury is precipitated.

*Action of Mercury Acetamide on Hydrazobenzene.*

A solution of 1.8 grams of hydrazobenzene in alcohol was treated with 3.2 grams of mercury acetamide dissolved in 75 per cent. spirit; a finely-divided precipitate of mercury was immediately produced, the pale yellow colour of the solution changing to red; there was no liberation of gas. The liquid was then gently heated, and, after a short interval, filtered, and evaporated on the water bath to a small bulk. Azobenzene crystallised from the diluted solution in characteristic, red plates melting at 68°. The equation,



represents the interaction of mercury acetamide and hydrazobenzene; the yield of azobenzene is practically quantitative.

*Action of Mercury Acetamide on Diazoamidobenzene.*

Ten grams of diazoamidobenzene were dissolved in alcohol, and added to a cold solution of 16 grams (1 mol.) of mercury acetamide in the same medium, and the copious, bright yellow precipitate which immediately separated was collected, washed, and drained on porous earthenware; the substance thus obtained crystallises from both chloroform and acetone in felted masses of thread-like, bright yellow

needles, and melts at  $242^{\circ}$ , at which temperature it decomposes vigorously; it yields mercury when distilled with lime.

0.1822 gave 22.1 c.c. of moist nitrogen at  $19^{\circ}$  and 764 mm.  $N = 14.01$ .

$C_{12}H_{11}N_3, Hg(NHAc)_2$  requires  $N = 13.64$  per cent.

The sparing solubility of the double compound in common solvents is remarkable. Chloroform was found the least inconvenient medium to employ, but 1,000 c.c. of the boiling solvent suffice to dissolve only 1 gram of the substance, which is scarcely soluble in the cold agent. A freshly prepared solution is pale yellow, but becomes deep brown on standing for several hours.

When treated with cold, dilute hydrochloric acid, the substance slowly dissolves, forming a cherry-red solution, in which alkalis and alkali carbonates produce a yellow precipitate. On adding a concentrated aqueous solution of platinum tetrachloride to the acid liquid, bright red needles are formed containing 31.93 per cent. of platinum. The identity of the salt, however, has not been established. Diazoamidobenzene platinumchloride,  $(C_{12}H_{11}N_3)_2, H_2PtCl_6$ , which one would expect to be formed, contains 24.19 per cent. of platinum, and explodes feebly at  $100^{\circ}$ ; the platinumchloride described above changes colour to pale brown at about  $100^{\circ}$ , but does not melt or decompose below  $233^{\circ}$ , when it chars and intumescs. A platinumchloride of diazoamidobenzene having the formula  $C_{12}H_{14}N_3, H_3PtCl_6$  would contain 32.01 per cent. of platinum.

#### *Action of Mercury Acetamide on Aniline.*

Mercury acetamide dissolves in warm aniline, and crystallises from the solution. The liquid darkens when boiled, but no separation of metal takes place, and on allowing the viscous solution to cool, mercury acetamide no longer crystallises out.

Thirty grams of the finely-divided mercury compound were dissolved in 35 grams of hot aniline, and the solution gently boiled during 5 minutes; it became dark brown, but remained clear, and did not deposit crystals on cooling. It was therefore treated with hot water, and distilled in steam until aniline no longer appeared in the distillate; the residual liquid was then boiled with animal charcoal, filtered, and evaporated on the water bath. The pale brown, viscous residue gradually hardened in the desiccator, forming an excessively tough, hygroscopic, opaque mass, in which crystals could not be detected. Although the product was very ill-defined, there can be little doubt that union between the two compounds had actually taken place; this is clearly shown by the following comparison of the substance with mercury acetamide.

Mercury acetamide.	Aniline derivative.
1. Caustic soda produces no change in cold solutions.	1. Caustic soda precipitates aniline.
2. Remains clear with dilute hydrochloric acid.	2. Dilute hydrochloric acid produces a copious, white precipitate.
3. Potassium iodide gives no precipitate.	3. Potassium iodide gives a bulky, dirty yellow, gelatinous precipitate.
4. Phenylhydrazine precipitates mercury which quickly collects in a globule; much heat is developed, and brisk effervescence takes place.	4. Phenylhydrazine precipitates mercury which remains in the form of a sticky, greenish deposit; feeble effervescence occurs, but rise of temperature is scarcely perceptible.
5. Hydrazine hydrochloride at first forms a yellow precipitate, which rapidly turns dark grey; brisk effervescence follows continued addition of the salt.	5. Hydrazine hydrochloride produces a copious, white precipitate, which undergoes no change in appearance, and does not yield gas with excess of the agent. Slight darkening occurs on boiling.
6. Hydroxylamine hydrochloride gives rise to a yellow precipitate which instantly turns dark grey; brisk effervescence and rise of temperature occur at the same time.	6. Hydroxylamine hydrochloride gives a dense white precipitate which remains unaltered by excess of the salt. No separation of mercury takes place when the substance is boiled with water.

The above tests were performed in each case with an aqueous solution of the substance in question.

From the experiments described in this paper, it will be recognised that mercury acetamide is an unexpectedly active substance. Its tendency to lose mercury in exchange for hydrogen is more freely displayed in presence of compounds in which that element is attached to nitrogen, particularly when an amino-, imino-, or hydroxyl group is to be found in the neighbourhood. It is distinguished by this behaviour as a convenient means of detecting primary and secondary hydrazines, and primary hydroxylamines, all of which resolve the substance into mercury and acetamide. Its capacity for producing additive compounds is quite astonishing. In addition to the products obtained from nitroso- $\beta$ -phenylhydroxylamine, aniline, and diazoamidobenzene, precipitates are formed on adding mercury acetamide to solutions of amidoazobenzene, methylamine and bornylamine hydrochlorides, alloxantin, resorcinol, and citric, tartaric, and oxamic acids; these substances represent a very large proportion of those with which experiments have been made, and doubtless other classes of compounds are capable of exhibiting similar behaviour.

Its oxidising—or, rather, dehydrogenising—influence is not confined to nitrogen derivatives, although these have been dealt with exclusively on the present occasion. An aqueous solution of quinol, for instance, rapidly becomes green when treated with mercury acetamide, from which the metal is precipitated, whilst the distinctive odour of quinone becomes perceptible. Pyrogallol yields an unstable, red product, which soon darkens, and finally becomes almost black, owing to separation of mercury. A cold solution of formic acid is indifferent towards the substance, but vigorous action takes place on boiling the liquid, which then deposits mercury. Formaldehyde is also unaffected at first, and remains clear for at least 1 minute when boiled with the mercury compound; the metal afterwards separates, however, forming a lustrous mirror, whilst yellow mercuric oxide remains suspended in the liquid.

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#### LXXIV.—*Sulphocamphylic Acid and Isolauronolic Acid,\* with Remarks on the Constitution of Camphor and of some of its Derivatives.*

By W. H. PERKIN, jun.

##### INTRODUCTION.

THE constitution of camphor still remains unsolved, in spite of the enormous amount of work which has been done during the last few years in almost every conceivable direction.

It is well known that camphor,  $C_{10}H_{16}O$ , on oxidation, yields *camphoric acid*,  $C_8H_{14}(COOH)_2$ , and that this acid, on further oxidation, yields *camphanic acid*,  $C_8H_{13}(OH)(COOH)_2$ , *camphoronic acid*,  $C_6H_{11}(COOH)_3$ , and other acids containing a smaller number of carbon atoms, but although the constitution of camphoronic acid has now been conclusively proved, there is still very considerable doubt as to the formulæ of camphoric acid and camphanic acid.

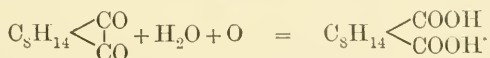
That the relationship existing between camphor and camphoric acid is a very close one is proved, not only by the fact that camphoric acid

\* Noyes (*Ber.*, 1895, 28, 549) proposes to alter the name of this acid to *cis-campholytic acid*, and to reserve the name *isolauronolic acid* for an isomeric acid which he has prepared. As, however, this is likely to cause much confusion, and there seems, in the meantime, no sufficient reason for the change, it has not been adopted in this paper.

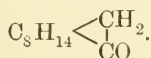
is so readily formed by oxidising camphor, but also by the formation of this acid from camphorquinone.

Claisen and Manasse (*Annalen*, 1893, 274—286) showed that camphor is readily converted into isonitrosocamphor,  $C_8H_{14} \begin{smallmatrix} \diagup C: NOH \\ | \\ CO \end{smallmatrix}$ , by treatment with amyl nitrite and sodium methoxide, and from this compound, by treatment with nitrous acid, they obtained camphorquinone,  $C_8H_{14} \begin{smallmatrix} \diagup CO \\ | \\ CO \end{smallmatrix}$ .

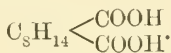
From camphorquinone, camphoric acid is readily obtained by the action of a solution of potash in methylic alcohol, hydrolysis and oxidation (due to the oxygen of the air) taking place simultaneously.



This series of simple reactions fully confirms the view, which has long been held by chemists, that camphor contains the group  $-CH_2 \cdot CO-$ , and that when it is converted into camphoric acid, this group is oxidised to two carboxyl groups.



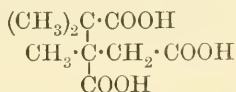
Camphor.



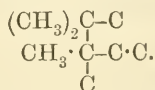
Camphoric acid.

It follows, therefore, that the constitution of camphor could be readily deduced from the constitution of camphoric acid, and this accounts for the great number of experiments which have been carried out with this acid.

Bredt's suggestion (*Ber.*, 1893, 26, 3049), that camphoronic acid has the constitution



was the first great advance in elucidating the formula of camphoric acid, and now that this constitution of camphoronic acid has been proved by the synthesis of the acid (Perkin and Thorpe, *Trans.*, 1897, 71, 1169), it can be stated with certainty that camphoric acid,  $C_{10}H_{16}O_4$ , contains 9 of its carbon atoms grouped in the following way.

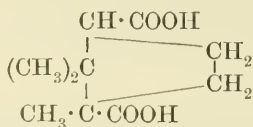


This fact disposes of a number of formulæ which had been suggested for camphoric acid, such as those of V. Meyer and Ballo, and of Tiemann,



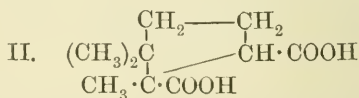
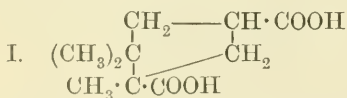
but, on the other hand, it does not afford a sufficient basis on which to build up a constitution for camphoric acid that shall not be open to question.

Arguing from the formula of camphoronic acid, Brecht (*loc. cit.*, p. 3049) has suggested that camphoric acid is probably represented thus.



and this well-known formula does undoubtedly explain a very large number of the reactions of the acid in a comparatively simple manner.

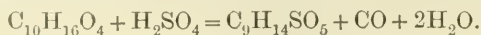
The investigation of sulphocamphylic acid and of isolauronolic acid, on which the author of this paper has been engaged during the last nine years, has, however, brought to light some facts which it seems almost impossible to explain with the aid of Brecht's formula, and this led the author, in 1896 (*Proc.*, 1896, p. 191\*), to suggest that the constitution of camphoric acid might equally well be represented by the following formulæ.



An acid having either of these formulæ could, on oxidation, yield camphoronic acid quite as well as an acid of the constitution suggested by Brecht.

It will furthermore be shown that the results obtained in the investigation of isolauronolic acid can only be readily explained on the assumption that formula I is the correct expression for the constitution of camphoric acid, and for this reason this formula has been adopted in this paper.

Among the many remarkable reactions in the camphor group, one of the most interesting is certainly the decomposition which takes place when camphoric acid is gently heated with concentrated sulphuric acid, the camphoric acid being converted almost quantitatively into *sulphocamphylic acid*, with evolution of carbonic oxide.



This decomposition was first observed by Walter (*Ann. Chim. Ph.*, 1843, [iii], 9, 177), and subsequently investigated by Kachler (*Ann-*

\* There is an unfortunate printer's error (in the abstract) in the first of these formulæ, two hydrogen atoms having been omitted.

alen, 1873, 169, 179) and Damsky (*Ber.*, 1887, 20, 2959), and for many years the formula for crystallised sulphocamphylic acid was supposed to be  $C_9H_{16}SO_6 + 2H_2O$ , a formula by which it is represented in the last edition of Beilstein's *Handbuch* (vol. i, p. 905).

During the course of further experiments on this acid, it was, however, clearly proved by Koenigs and Meyer (*Ber.*, 1894, 27, 3466), as well as by the author (*Proc.*, 1895, p. 23), that sulphocamphylic acid in reality has the formula  $C_9H_{14}SO_5$ , and that it crystallises with  $3H_2O$ , two of which are given off at  $100^\circ$  and the third at about  $110^\circ$ , and the proof of this fact may be briefly stated as follows.

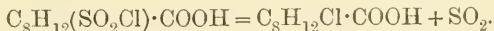
When the silver salt of sulphocamphylic acid is treated with methylic iodide, the dimethylic salt is obtained, and this, on analysis, was shown to have the formula  $C_9H_{12}SO_5(CH_3)_2$  (Koenigs and Meyer, *loc. cit.*, p. 3467).

Similarly, the potassium salt of sulphocamphylic acid, when treated with phosphorus pentachloride or pentabromide, yields the *sulphochloride* or *sulphobromide*, and these, on analysis, give numbers agreeing sharply with the formulæ  $C_9H_{13}O_2(SO_2Cl)$  and  $C_9H_{13}O_2(SO_2Br)$ , formulæ which clearly prove that the composition of sulphocamphylic acid must be  $C_9H_{13}O_2 \cdot SO_3H$ , and not  $C_9H_{15}O_3 \cdot SO_3H$ , as was at first supposed.

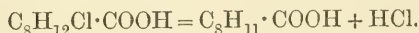
Furthermore, it has been conclusively shown by the analysis of a number of metallic salts, as well as by the formation of the dimethylic salt mentioned above, that sulphocamphylic acid is dibasic, and therefore its formula may be written  $C_8H_{12}(SO_3H) \cdot COOH$ .

The investigation of the sulphochloride and sulphobromide of sulphocamphylic acid has given very interesting results, some of which are described in this paper; others are reserved for a future communication.

The sulphochloride\* is a beautiful, crystalline substance, which melts at  $168^\circ$ , and is at the same time decomposed with evolution of sulphur dioxide and formation of a new acid,  $C_8H_{12}Cl \cdot COOH$ , melting at  $106^\circ$ .



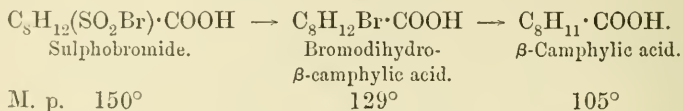
This acid has been called *chlorodihydro-β-camphylic acid*, because, on prolonged treatment with alcoholic potash, it is converted into β-camphylic acid,† with elimination of hydrogen chloride,



\* The decompositions described here are exactly similar to those which Kipping and Pope (*Trans.*, 1895, 67, 371) have used with such success in the preparation of π-halogen derivatives of camphor.

† Compare *Proc.*, 1893, 109; 1895, 23; 1896, 189. A detailed description of this very interesting acid will, it is hoped, form the subject of a future communication.

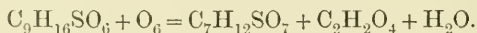
In a similar manner, the sulphobromide of sulphocamphylic acid, when heated above its melting point, decomposes, with evolution of sulphur dioxide and formation of *bromodihydro-β-camphylic acid*, and this acid is decomposed by alcoholic potash in the same way as the corresponding chloro-acid, yielding again *β-camphylic acid*.



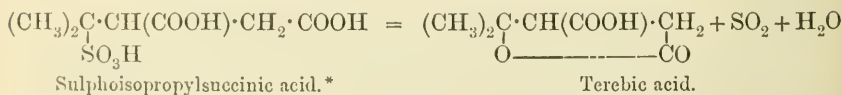
Since, then, it is clear from the above that sulphocamphylic acid must be represented by the formula  $\text{C}_8\text{H}_{12}(\text{SO}_3\text{H})\cdot\text{COOH}$ , the next important matter is to discuss all the evidence which has a bearing on the further arrangement of the atoms in this molecule.

It has been frequently found in the camphor and terpene series that the study of the behaviour of these substances and their derivatives towards oxidising agents has given valuable clues to their constitution, and in the case of sulphocamphylic acid also, although in a less degree than might have been expected, important results have been obtained in this way.

Kachler (*Annalen*, 1873, 169, 181), who was the first to oxidise sulphocamphylic acid, found that, when heated with nitric acid, it is converted into oxalic acid and a beautifully crystalline tribasic acid, which he called *sulphopimelic acid*, and the formation of which he expressed by the equation



Subsequently, Koenigs and Hoerlin (*Ber.*, 1893, 26, 2045) carefully investigated this sulphopimelic acid, and found that at 160—170° it is decomposed with evolution of sulphur dioxide and formation of terebic acid; they therefore considered that Kachler's acid must be sulphoisopropylsuccinic acid, in which case the formation of terebic acid is readily understood.



These chemists also found that small quantities of dimethylmalonic acid,  $(\text{CH}_3)_2\text{C}(\text{COOH})_2$ , are produced during the oxidation of sulphocamphylic acid with nitric acid, an important result, since the formation of this acid indicates that sulphocamphylic acid contains the group  $-\text{C}\cdot\text{C}(\text{CH}_3)_2\cdot\text{C}-$ .

\* In studying the possible formulæ for sulphocamphylic acid, it is very difficult to understand how the sulphonic group in sulphopimelic acid can occupy the position given to it here.

Sulphocamphylic acid is also readily oxidised by potassium permanganate in alkaline solution, yielding a variety of very interesting products, which have been carefully investigated by the author of this paper, but the description of these must be reserved for a future communication.

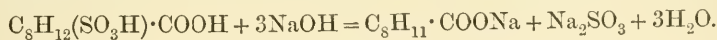
*Action of Heat on Sulphocamphylic Acid. Formation of Isolaunonic Acid,  $C_8H_{13} \cdot COOH$ .*

When sulphocamphylic acid is heated in small quantities, or distilled with superheated steam, it undergoes a very remarkable decomposition, yielding isolaunonic acid and sulphuric acid (Koenigs and Hoerlin, *Ber.*, 1893, 26, 813; Perkin, *Centralblatt.*, 1893, ii, 50),

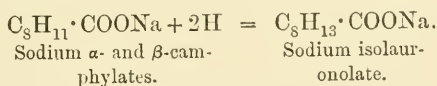


but, unfortunately, at the high temperature necessary for the decomposition, the sulphuric acid formed destroys much of the sulphocamphylic acid, and the yield of isolaunonic acid obtained hardly ever exceeds 10 per cent. of the theoretical. It was subsequently discovered by the author that isolaunonic acid may be obtained in comparatively large quantities by fusing sulphocamphylic acid in a cast iron pot with caustic soda, a remarkable result, which may be explained as follows.

In the first place, the sulphocamphylic acid is decomposed by the fusion with soda, with formation of the sodium salts of the isomeric  $\alpha$ - and  $\beta$ -camphylic acids,  $C_8H_{11} \cdot COOH$  (Perkin, *Proc.*, 1893, 109; 1895, 23).



The iron of the vessel in which the fusion is carried out then reduces these sodium salts, and the product, which is coloured dark brown by the ferric oxide which it holds in suspension, contains the sodium salt of isolaunonic acid.



Although this method is a considerable improvement on the dry distillation of sulphocamphylic acid, it is, nevertheless, a very laborious process, and the best way for preparing isolaunonic acid is undoubtedly that worked out by Blanc (*Bull. Soc. Chim.*, [iii], 15, 1191), which consists in treating a solution of camphoric anhydride in chloroform with aluminium chloride, when the following remarkable decomposition takes place.



Another method of formation of isolauronolic acid direct from camphoric acid, to be discussed later in this paper, is that discovered by Walker (Trans., 1893, 63, 495). Walker submitted orthoethylic sodium camphorate to electrolysis, and obtained in this way, besides ethylic campholytate, an isomeric ethylic salt boiling at 135—140° (15mm.), which he first called diethylic camphothetate, but which was subsequently (Trans., 1895, 67, 347) shown to be the ethylic salt of isolauronolic acid.

Lastly, Noyes (Ber., 1894, 65, 917; 1895, 67, 549) has obtained isolauronolic acid by the following series of reactions.

The imide of camphoric acid,  $C_8H_{14} \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{CO} \end{smallmatrix} NH$ , when treated with potash, yields  $\beta$ -camphoraminc acid,  $C_8H_{14}(CONH_2) \cdot COOH$ , and this, by the action of sodium hypobromite, is converted into dihydroaminocampholytic acid,  $C_8H_{14}(NH_2) \cdot COOH$ ; nitrous acid converts this amido-acid into Walker's campholytic acid, which, when boiled with dilute sulphuric acid, undergoes molecular change, yielding isolauronolic acid.

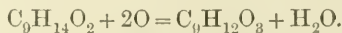
The determination of the constitution of isolauronolic acid is of great importance, for the following reasons.

1. It is formed from camphoric anhydride by elimination of CO.
2. It is formed from sulphocamphylic acid by heat.
3. It is reconverted into sulphocamphylic acid by treatment with sulphuric acid (see p. 835).

From these facts, it will be seen that isolauronolic acid is closely related to camphoric acid on the one hand, and to sulphocamphylic acid on the other, so that the determination of the constitution of this acid must throw much light on the question of the constitution of camphoric and of sulphocamphylic acids.

*Oxidation of Isolauronolic Acid. Formation of Isolauronic Acid,*  
 $C_9H_{12}O_3$ .

If a drop of potassium permanganate solution is added to a solution of isolauronolic acid in dilute sodium carbonate, the colour is instantly discharged, even at 0°; and, on investigating this reaction, it is found that the first product of the oxidation is an acid of the formula  $C_9H_{12}O_3$ .



This new acid, which was first described by Koenigs and Meyer (Ber., 1894, 27, 3467), and called by them *isolauronic acid*, melts at 133°, and differs from isolauronolic acid in being readily soluble in hot water; it is a ketonic acid, and forms the following well characterised derivatives.



<i>Oxime</i> ....	$\text{COOH} \cdot \text{C}_7\text{H}_{11} \cdot \text{C}:\text{NOH}$	m. p. $222^\circ$
<i>Semicarbazone</i> .....	$\text{COOH} \cdot \text{C}_7\text{H}_{11} \cdot \text{C}:\text{N} \cdot \text{NH} \cdot \text{CONH}_2$	„ $248$
<i>Phenylhydrazone</i> *	$\text{COOH} \cdot \text{C}_7\text{H}_{11} \cdot \text{C}:\text{N} \cdot \text{NH} \cdot \text{C}_6\text{H}_5$	„ $199$

*Oxidation of Isolauroic Acid.*—Although stable to permanganate at temperatures below  $0^\circ$ , isolauroic acid is readily oxidised by this agent at ordinary temperatures, as also by a mixture of potassium dichromate and sulphuric acid at  $90$ — $95^\circ$ , the principal substances formed being

$\gamma$ -Dimethylacetylbutyric acid,  $\text{CH}_3 \cdot \text{CO} \cdot \text{C}(\text{CH}_3)_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{COOH}$ .

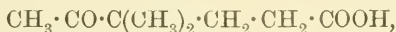
$\alpha$ -Dimethylglutaric acid,  $\text{COOH} \cdot \text{C}(\text{CH}_3)_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{COOH}$ .

$\alpha$ -Dimethylsuccinic acid,  $\text{COOH} \cdot \text{C}(\text{CH}_3)_2 \cdot \text{CH}_2 \cdot \text{COOH}$ .

All these substances afford important evidence as to the constitution of isolauroic acid, but there can be no doubt, as will be shown later, that it is the first named which is especially valuable in this connection.

Acetyldimethylbutyric acid is identical with the acid which Tiemann (*Ber.*, 1895, 28, 2176) obtained by the oxidation of  $\beta$ -dihydroxydihydrocampholenic acid, and which he named dimethyl-3-hexanon-2 acid.

That this acid has the constitution



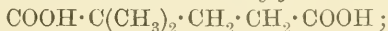
is proved by the following considerations.

1. It is a ketonic acid, as is shown by the fact that it yields a well characterised oxime and semicarbazone.

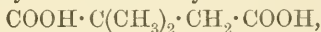
2. When reduced with sodium amalgam, it is converted into a lactone,  $\text{CH}_3 \cdot \underset{\text{O}}{\text{CH}} \cdot \text{C}(\text{CH}_3)_2 \cdot \text{CH}_2 \cdot \underset{\text{CO}}{\text{CH}_2}$  (b. p.  $239$ — $241^\circ$ ), a fact which in-

dicates that the CO group is either in the  $\gamma$ - or  $\delta$ - position.

3. Sodium hypobromite readily reacts with the acid, with separation of bromoform and formation of  $\alpha\alpha$ -dimethylglutaric acid,

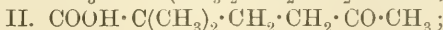
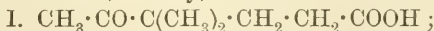


this shows that the ketonic acid contains the group  $\text{CH}_3 \cdot \text{CO}$ . The dimethylglutaric acid formed in this way melts at  $84^\circ$ , and is isomeric with  $\beta\beta$ -dimethylglutaric acid,  $\text{COOH} \cdot \text{CH}_2 \cdot \text{C}(\text{CH}_3)_2 \cdot \text{CH}_2 \cdot \text{COOH}$  (m. p.  $101^\circ$ ; Goodwin and Perkin, *Trans.*, 1896, 69, 1473), and since on oxidation the former yields  $\alpha\alpha$ -dimethylsuccinic acid,



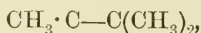
it can only have the constitution  $\text{COOH} \cdot \text{C}(\text{CH}_3)_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{COOH}$ .

4. From the formula of  $\alpha\alpha$ -dimethylglutaric acid, two ketonic acids,  $\text{C}_8\text{H}_{14}\text{O}_3$ , may be derived, namely,



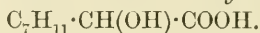
\* Carl Meyer (*Inaugural Dissertation Munich*, 1895, p. 38).

but there can be no doubt that formula I represents the constitution of the acid obtained from isolauronic acid, because throughout the whole camphor series there is overwhelming evidence that the three methyl groups contained in this substance and its derivatives are united to neighbouring carbon atoms forming the complex



a condition which is satisfied by formula I, but not by II.

*Reduction of Isolauronic Acid to Dihydroisolauronic Acid,*



The action of sodium amalgam on isolauronic acid was first investigated by Carl Meyer (*Dissertation Munich*, 1895, p. 45) who obtained in this way two products.

1. A lactone,  $\text{C}_9\text{H}_{14}\text{O}_2$ , melting at  $47-50^\circ$  and yielding on hydrolysis a hydroxy-acid melting at  $143^\circ$ .

2. An acid melting at  $81^\circ$  which does not yield a lactone, and which, on analysis, gave the following numbers.

Found (mean of three analyses) C = 62.95 ; H = 8.66.

$\text{C}_9\text{H}_{14}\text{O}_3$  requires C = 63.53 ; H = 8.23.

$\text{C}_9\text{H}_{16}\text{O}_3$      ,,     C = 62.71 ; H = 9.30.

These results led Meyer to conclude that the acid melting at  $81^\circ$  was a mixture of two acids,  $\text{C}_9\text{H}_{14}\text{O}_3$  and  $\text{C}_9\text{H}_{16}\text{O}_3$ , which could not be separated by crystallisation.

As the investigation of the behaviour of isolauronic acid on reduction is a matter of fundamental importance in determining the constitution of this acid, a great many experiments on this subject have been made by the author, the results of which differ considerably from those obtained by Carl Meyer. In the first place, Carl Meyer's experiments were repeated exactly as he described them, using isolauronic acid which had been very carefully purified by repeated crystallisation, but no trace of a solid lactone could be detected in the product, which consisted of a beautifully crystalline acid melting at  $88-89^\circ$ , and on analysis gave numbers agreeing sharply with those required by the formula  $\text{C}_9\text{H}_{14}\text{O}_3$ .

Found (mean of two analyses) C = 63.36 ; H = 8.21.

$\text{C}_9\text{H}_{14}\text{O}_3$  requires C = 63.53 ; H = 8.23.

The conditions of reduction were then varied, but in all cases it was found that the isolauronic acid had been converted almost quantitatively into the acid  $\text{C}_9\text{H}_{14}\text{O}_3$ , which, since it is formed by the addition of two atoms of hydrogen to isolauronic acid, has been called *dihydroisolauronic acid*.

The solution of dihydroisolauronic acid in sodium carbonate does

not decolorise permanganate except on long standing, showing that the acid is a saturated acid, and this is confirmed by the fact that the acid does not combine with bromine, or with hydrogen bromide, and that it is not further reduced even when its alkaline solution is boiled with sodium amalgam.

Since dihydroiselauronic acid is formed by the reduction of the ketonic acid iselauronic acid, it is evident that it must be a hydroxy-acid, and the next important point was to determine whether it was capable of forming a lactone, since, in this way, valuable evidence as to the relative positions of the hydroxyl and carboxyl groups, and indirectly as to the position of the CO and COOH in iselauronic acid, might be obtained.

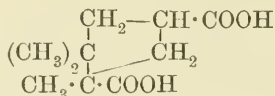
This matter has been most carefully investigated, but it was not found possible to obtain even traces of a lactone by boiling the hydroxy-acid with dilute sulphuric acid; and, indeed, the hydroxy-acid may be distilled without decomposition; it may therefore be safely stated that *dihydroiselauronic acid is incapable of forming a lactone*.

This statement may, at first sight, appear to be at variance with the results obtained by Carl Meyer (*Dissertation*, p. 46), who, by the reduction of iselauronic acid, obtained, as mentioned above, small quantities of a lactone,  $C_9H_{14}O_2$ , melting at  $47-50^\circ$ , and which on hydrolysis yielded an acid melting at  $143^\circ$ . The principal product of the reduction was, however, a hydroxy-acid melting at  $81^\circ$ , and yielding on analysis numbers agreeing with those required by a mixture of acids,  $C_9H_{14}O_3$  and  $C_9H_{16}O_3$ , and there can now be no doubt that this acid was simply slightly impure dihydroiselauronic acid (m. p.  $88^\circ$ ). Since Meyer's acid melting at  $81^\circ$  was isolated from the product of the reduction of iselauronic acid after this had been boiled with dilute acids, it is evident that his acid is also incapable of forming a lactone, and in this respect Meyer's experiments agree with those of the author. With regard to the nature of the lactone melting at  $47-50^\circ$  and yielding, on hydrolysis, the acid melting at  $143^\circ$ , it seems extremely probable that this was *campholactone*,  $C_9H_{14}O_2$ , which melts at  $50-51^\circ$ , and which on hydrolysis with baryta yields *campholactonic acid*,  $C_9H_{16}O_3$ , melting at  $143^\circ$ ;<sup>\*</sup> the few properties of his lactone which Meyer mentions confirm this view. Since, however, campholactone is the lactone corresponding to lauronic acid (see p. 815), it is exceedingly difficult to understand its formation by the reduction of a derivative of iselauronic acid.

<sup>\*</sup> According to Woringer (*Annalen*, 1885, **227**, 10) campholactonic acid is precipitated as an oil on acidifying the solution of its barium salt; the author, however, in conjunction with Mr. R. W. Collinson, has obtained the acid by this method in the form of beautiful prismatic crystals melting at  $143^\circ$ . An account of this interesting acid is reserved for a future communication.

*The Constitution of Isolauronic Acid, of Isolauronic Acid, and of Sulphocamphylic Acid, with remarks on the Constitution of Camphor and of Camphoric Acid.*

It has already been stated that, in the opinion of the author, the results obtained in this investigation can best be explained on the assumption that camphoric acid has the constitution represented by the formula



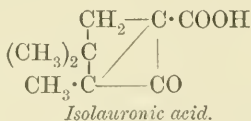
and in giving the reasons for this statement it will be best in the first place to discuss the constitution of isolauronic acid, in doing which the principal points to be borne in mind are,

1. Isolauronic acid, on oxidation, yields  $\gamma$ -dimethylacetylbutyric acid,  $\text{CH}_3 \cdot \text{CO} \cdot \text{C}(\text{CH}_3)_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{COOH}$ .

2. Isolauronic acid is a monobasic ketonic acid containing the ketonic group in the  $\beta$ -position relatively to the carboxyl group. This is proved by the fact that the dihydroisolauronic acid obtained by its reduction is incapable of forming a lactone.

3. Since dihydroisolauronic acid distils unchanged, it cannot contain the group  $-\text{CH} \cdot \text{CH}(\text{OH})-$ , because acids containing that group, on distillation, lose water with formation of the corresponding unsaturated acids. Isolauronic acid itself must, therefore, contain the group  $\text{COOH} \cdot \text{C} \cdot \text{CO} \cdot \text{C}$ , the free bonds of which must all be united to carbon.

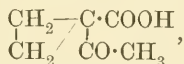
From the formula of camphoric acid given above an expression for the constitution of isolauronic acid can be easily deduced which will satisfy these conditions and explain all the known properties of the acid, namely,



This formula, which appears to the author to be the only possible formula for isolauronic acid, represents the acid as a  $\beta$ -ketonic acid, and to this the objection might be raised that the acid gives no coloration with ferric chloride, and that when heated it does not decompose with evolution of carbon dioxide. The reply to the first objection is that  $\beta$ -ketonic acids, or their ethereal salts, which have both  $\alpha$ -hydrogen atoms replaced by radicles do not appear to give a coloration with ferric chloride, thus, for example, the author finds that ethylic dimethyl-acetoacetate,  $\text{CH}_3 \cdot \text{CO} \cdot \text{C}(\text{CH}_3)_2 \cdot \text{COOC}_2\text{H}_5$ , does not give a coloration with ferric chloride.

The relatively great stability of isolauronic acid is also quite easily explained. The ease with which  $\beta$ -ketonic acids are decomposed by heat or alkalis with elimination of carbon dioxide depends very much on their constitution.

Thus acetoacetic acid,  $\text{CH}_3 \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{COOH}$ , and methylacetoacetic acid,  $\text{CH}_3 \cdot \text{CO} \cdot \text{CH}(\text{CH}_3) \cdot \text{COOH}$ , are oils which decompose slowly at ordinary temperatures with evolution of carbon dioxide, whereas dimethylacetoacetic acid,  $\text{CH}_3 \cdot \text{CO} \cdot \text{C}(\text{CH}_3)_2 \cdot \text{COOH}$ , is solid, and although still very easily decomposed, it is distinctly more stable than the other two acids. These three acids are furthermore readily decomposed in the same manner by boiling with potash. When, however, the carboxyl and acetyl groups in such compounds are attached to a closed chain, as in the case of acetyltrimethylenecarboxylic acid,

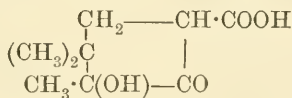


an acid which has a somewhat similar formula to that suggested for isolauronic acid, the stability of the molecule may be, but is not always, enormously increased. Acetyltrimethylenecarboxylic acid, for example, may be boiled with potash for hours without decomposition, and the free acid is only slowly decomposed into carbon dioxide and acetyltrimethylene even at  $180-200^\circ$ .

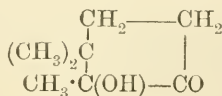
If, then, the introduction of one closed chain into the molecule can bring about such an extraordinary change in stability, it is not remarkable that this stability should be still more pronounced in a substance like isolauronic acid, the formula of which is represented above, not only as containing two closed chains, but also as having no  $\alpha$ -hydrogen atoms.

The formation of dimethylacetylbutyric acid from isolauronic acid may be readily explained with the aid of this formula as follows.

In the first place, the trimethylene ring is split with the addition of the elements of water and formation of an intermediate substance of the formula

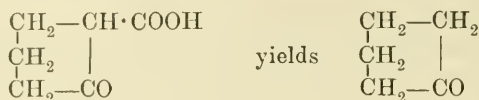


and this being a  $\beta$ -ketonic acid with one  $\alpha$ -hydrogen atom not replaced, may be assumed to decompose readily with evolution of carbon dioxide and formation of the substance

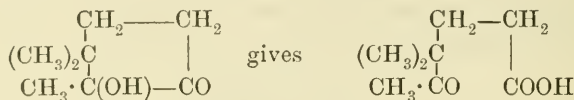




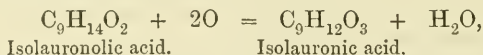
Thus Dieckmann (*Ber.*, 1894, 27, 103) has shown that ethylic  $\beta$ -ketopentamethylenecarboxylate, a substance of very similar constitution to the "intermediate" substance, is readily and quantitatively decomposed on hydrolysis, with formation of ketopentamethylene.



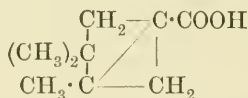
Lastly, the ketonic substance of the formula given above, being produced in the presence of oxidising agents, is readily converted into acetyldimethylbutyric acid.



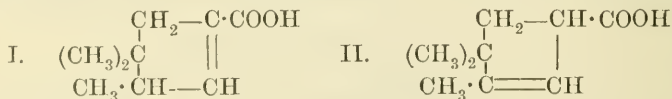
Assuming that the constitution given to isolauronic acid is correct, the next point is to deduce from this the formula for isolauronic acid. This at first sight seems to be a simple matter, since isolauronic acid is formed from isolauronic acid by replacing two hydrogen atoms by an oxygen atom, thus.



and therefore the formula for isolauronic acid, which suggests itself at once, is



But this formula would represent isolauronic acid as a saturated acid, and yet in many of its properties it behaves like an unsaturated acid, so that there are grounds for assuming that one of the alternative formulæ



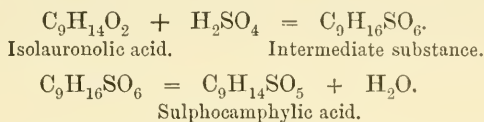
is more probable.

It must, however, be remembered that it is sometimes a matter of the greatest difficulty to distinguish between unsaturated substances and trimethylene derivatives, since the latter frequently form additive compounds with bromine, hydrogen bromide, and, less readily, with hydrogen; but trimethylene derivatives are, as a rule, stable towards permanganate at ordinary temperatures.

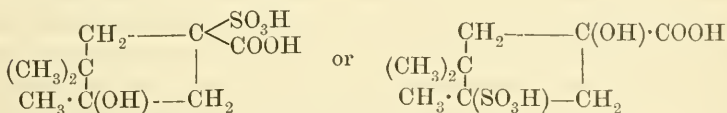
In favour of the unsaturated formula for isolaunonic acid is undoubtedly the fact that this acid instantly reduces permanganate in alkaline solution even at  $0^\circ$ , that it forms a dibrom-additive product when its solution in chloroform is treated with bromine at  $0^\circ$  and in the dark (Noyes, *Ber.*, 1895, 28, 552), and that it combines with hydrogen bromide;\* on the other hand, it is only reduced with difficulty by prolonged treatment with boiling amyl alcohol and sodium, remaining unchanged when its alkaline solution is boiled with sodium amalgam.

But the chief argument against the trimethylene formula is this, that this formula does not explain the fact that isolaunonic acid is obtained from sulphocamphylic acid by the action of heat, and is again converted into this acid by treatment with sulphuric acid.

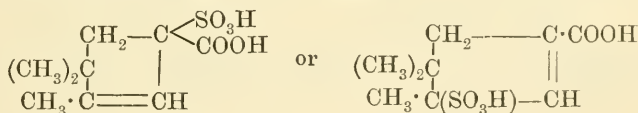
It seems probable that the latter most interesting formation of sulphocamphylic acid takes place in two stages.



Assuming, then, that isolaunonic acid contains a trimethylene ring, the addition of sulphuric acid can only take place by the splitting of the trimethylene ring, and we shall then get for the formula of the intermediate substance either



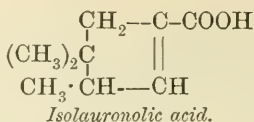
and the constitution of sulphocamphylic acid deduced from these formulæ would be either



If, now, we remove  $\text{SO}_3$  from these formulæ to produce isolaunonic acid, we can quite easily see that the acid may have one of the two unsaturated formulæ given on p. 808, but the reconstruction of the trimethylene formula by eliminating  $\text{SO}_3$  involves an intramolecular change for the occurrence of which little probability exists.

If, then, isolaunonic acid is an unsaturated acid, the question at once arises whether its constitution is represented by formula I or II (p. 808), and there can be no doubt that the former, that is, the formula

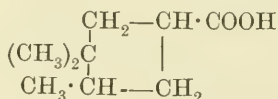
\* Noyes (private communication).



best explains the properties of this acid.

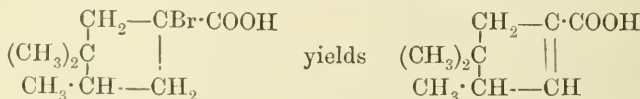
Isolauronolic acid distils without decomposition, and when boiled with dilute sulphuric acid does not yield a lactone. It cannot, therefore, be a  $\beta\gamma$ -unsaturated acid such as is represented in formula II, since an acid of this constitution would readily yield a lactone under these conditions; and other properties of this acid, which are explained in more detail in the following pages, lead to the same conclusion, namely, that isolauronolic acid is an  $\alpha\beta$ -unsaturated acid.

Perhaps the most striking confirmation of this view of the constitution of isolauronolic acid is the following. When reduced by amylic alcohol and sodium, isolauronolic acid,  $\text{C}_9\text{H}_{14}\text{O}_2$ , yields dihydro-isolauronolic acid,  $\text{C}_9\text{H}_{16}\text{O}_2$ , the double bond being reduced, and it is obvious that the constitution of this acid will be represented by the formula

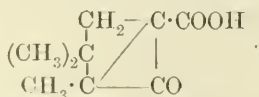


quite independently of whether formula I or II (p. 808) is taken as the constitution of isolauronolic acid.

But it has been shown by Noyes (*Amer. Chem. J.*, 1896, 18, 689), and independently by the author, that dihydroisolauronolic acid, on bromination, behaves quite normally, and yields a monobromo-derivative in which the bromine atom is doubtless in the  $\alpha$ -position. Now, when this bromo-derivative is treated with alcoholic potash, isolauronolic acid is quantitatively produced, hydrogen bromide being eliminated between the  $\alpha$ - and  $\beta$ -carbon atoms in the usual way.

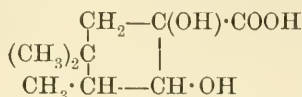


But it must be confessed that, although this formula is so very satisfactory in many ways, it is not quite easy to deduce from it the formula for isolauronic acid which was advocated on p. 806, namely,

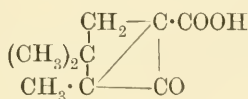


It is, of course, possible to do this by assuming that the oxidation of isolauronolic acid by permanganate takes place in the following stages,

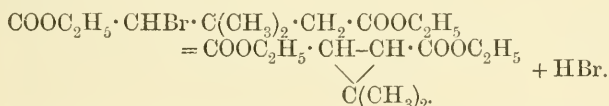
I. The oxidation proceeds in the usual way, with formation of the intermediate dihydroxy-acid of the formula



II. The  $\text{CH}\cdot\text{OH}$  group is oxidised to  $\text{CO}$ , and at the same time water is eliminated, and the trimethylene ring is formed, these changes resulting in the formula of isolauronic acid,

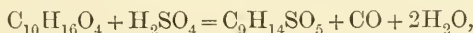


The formation of a trimethylene ring in this way, during the course of an oxidation, is certainly unusual; but there are grounds for assuming that the trimethylene ring may be produced much more easily than used to be thought possible. The above change is, for example, hardly more remarkable than the formation of the *ethylic* salt of *caronic acid* from *ethylic*  $\alpha$ -bromo- $\beta$ -dimethylglutarate, by simply warming with alcoholic potash (Perkin and Thorpe, *Trans.*, 1897, p. 107).

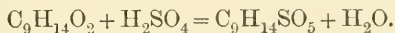


It has already been shown that it is improbable that the relationship existing between isolauronic acid and sulphocamphylic acid can be explained on the basis of the trimethylene formula, and it remains to be shown that, with the aid of the unsaturated formula for isolauronic acid, this difficulty can be got over.

Sulphocamphylic acid is formed, as is well-known, by the action of sulphuric acid on camphoric acid or camphoric anhydride,



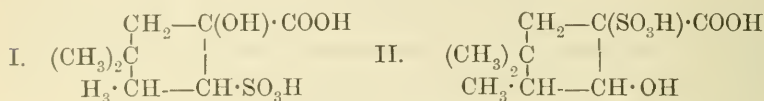
and it is also produced quantitatively when isolauronic acid is warmed with concentrated sulphuric acid,



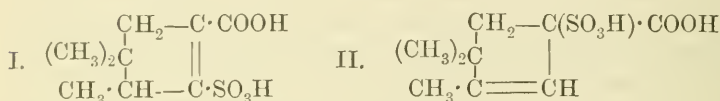
If it be remembered that camphoric anhydride is readily converted into isolauronic acid with evolution of carbon monoxide when its solution in chloroform is treated with aluminium chloride in the cold, it seems very probable that, in the formation of sulphocamphylic acid from camphoric anhydride, isolauronic acid is first produced, and that this then reacts with the sulphuric acid.

The formation of sulphocamphylic acid in this way may be assumed to take place in two stages.

In the first place, the sulphuric acid is added on at the double bond in the isolauronolic acid, a change which may take place in two ways, with the formation of the following substances.

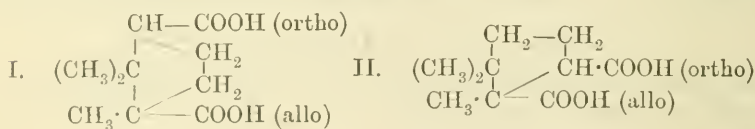


The large excess of sulphuric acid which it is necessary to have present, then acts as a dehydrating agent, water is eliminated, and thus two expressions of the constitution of sulphocamphylic acid are obtained, namely,



Since, however, the elimination of  $\text{SO}_3$  and formation of isolauronolic acid can only be explained by the aid of formula I, this view of the constitution of sulphocamphylic acid has been adopted in this paper. This formula is also in accord with all the known reactions of sulphocamphylic acid, thus, for example, it represents the substance as being an unsaturated acid, and this accounts for the fact that the acid is at once oxidised by permanganate in alkaline solution even at temperatures considerably below  $0^\circ$ .

From the above, it will be seen that the formation and properties of isolauronic, isolauronolic, and sulphocamphylic acids, can be explained with the aid of the author's formula for camphoric acid, and it remains to be shown that the other possible formulæ for camphoric acid, namely, Bredt's formula I and the formula II,



which was at one time considered probable by the author (Proc., 1896, p. 191), do not give an explanation of the formation and properties of these acids.

In the formation of isolauronolic acid from camphoric acid, by the action of sulphuric acid or aluminum chloride, the elements of formic acid are eliminated,





or, in other words, one of the carboxyl groups in the camphoric acid is removed, and the important point is to determine which of the two carboxyl groups remains.

In order to do this, it will be convenient to adopt the nomenclature used by Brühl, Walker, and others, and to represent the carboxyl groups as *ortho* and *allo* in the way shown in the above formulæ.

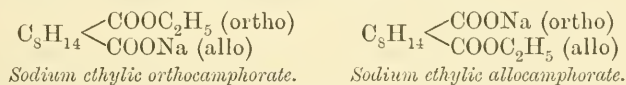
Now there are two series of unsaturated acids which can be obtained from camphoric acid by the elimination of formic acid, according to whether the *ortho*- or the *allo*-carboxyl group is removed during the process, namely.

1. The series the chief member of which is lauronolic acid,  $C_8H_{13} \cdot COOH$ .

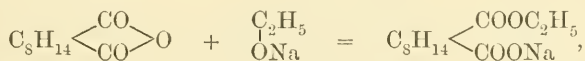
2. The series the chief member of which is isolauronolic acid  $C_8H_{13} \cdot COOH$ .

And it can be proved that the former series contain the *allo*-the latter the *ortho*-carboxyl group of the original camphoric acid molecule.

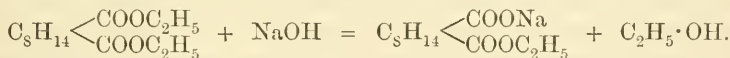
In order to make this clear, it will be necessary to refer briefly to Walker's and Walker and Henderson's important researches on the electrolysis of the sodium and potassium salts of the ethylic *ortho*- and *allo*-camphorates (Trans., 1893, 63, 495; 1895, 67, 337; 1896, 69, 748). Camphoric acid yields two isomeric sodium ethylic salts which may be provisionally represented by the formulæ



The first of these is formed by the addition of sodium ethoxide to camphoric anhydride,



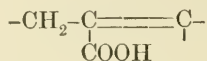
and the second by the partial hydrolysis of ethylic camphorate,



When sodium ethylic *ortho*-camphorate is electrolysed, the product is found to contain the ethereal salts of two isomeric unsaturated acids of the formula  $C_8H_{13} \cdot COOH$ ; one of these acids is isolauronolic acid, and the other has been named campholytic acid. Campholytic acid combines directly with bromine, yielding a dibromide,  $C_8H_{13}Br_2 \cdot COOH$ , and this when treated with sodium carbonate is decomposed with formation of a bromo-derivative of an unsaturated hydrocarbon,



and since this decomposition is shown only by the dibrom-additive products of  $\alpha\beta$ -unsaturated acids, Walker concludes that campholytic acid contains the group



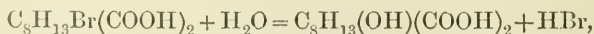
Noyes (*Ber.*, 1895, 28, 548) subsequently showed that campholytic acid is converted into the isomeric isolauronolic acid by boiling with dilute sulphuric acid; it is therefore probable that these two acids have the same structural formula and are simply stereoisomeric.

Similarly, sodium ethylic *allo*-camphorate yields, on electrolysis, the ethereal salts of two isomeric unsaturated acids,  $\text{C}_8\text{H}_{13} \cdot \text{COOH}$ , namely, *allo*-campholytic acid, and a small quantity of an oily acid which is possibly lauronolic acid. Both *allo*-campholytic acid and lauronolic acid, when boiled with dilute acids, yield the isomeric campholactone; they are therefore probably stereoisomeric, and since the formation of a lactone in this way is characteristic of  $\beta\gamma$ -unsaturated acids, it is assumed that both these acids contain the group  $\text{>C} \cdot \underset{\text{I} \diagup}{\text{C}} \cdot \text{C} \cdot \text{COOH}$ .

It is obvious from the method of formation that in the two series of unsaturated acids,  $\text{C}_8\text{H}_{13} \cdot \text{COOH}$ , namely, (*a*) lauronolic acid and *allo*-campholytic acid, (*b*) isolauronolic acid and campholytic acid, the acids all contain one of the carboxyl groups of the original camphoric acid molecule, and that the carboxyl group remaining in series *a* is a different one from that in series *b*.

It has been assumed in the above that the lauronolic series contains the *allo*-carboxyl group, and the isolauronolic series the *ortho*-carboxyl group, and it can be shown in several ways that this is the case, but for the purposes of this paper the formation of lauronolic acid from camphanic acid need only be considered.

When camphoric acid,  $\text{C}_8\text{H}_{14}(\text{COOH})_2$ , is brominated, the reaction takes place in the normal way with formation of the anhydride of bromocamphoric acid,  $\text{C}_8\text{H}_{13}\text{Br}(\text{COOH})_2$ , and it is obvious that the substitution must take place at the  $\alpha$ -carbon atom connected with the *ortho*-carboxyl group (pp. 812, 815), since the  $\alpha$ -carbon atom connected with the *allo*-carboxyl group has no hydrogen attached to it. When bromocamphoric anhydride is treated with dilute alkalis, it undergoes decomposition, yielding *camphanic acid*, the lactone of hydroxycamphoric acid,

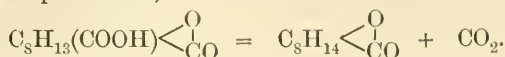


together with lauronolic acid, this acid being produced by the elimination of carbon dioxide and hydrogen bromide, thus,



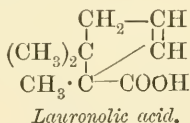
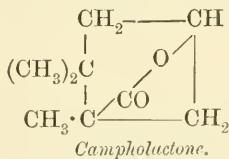
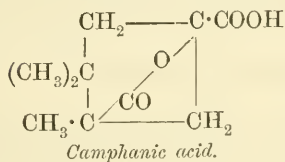
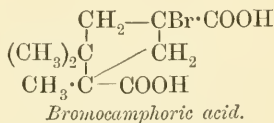
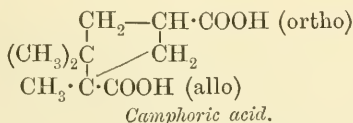
(Aschan, *Ber.*, 1894, 27, 3504).

When camphanic acid\* is distilled, it readily loses carbon dioxide and yields campholactone,



In this decomposition, the carboxyl group which is eliminated must be the *ortho*- one, since lactone formation cannot take place between a hydroxy-group and a carboxyl group when both are attached to the same carbon atom. Now lauronic acid is readily converted into campholactone by boiling with dilute sulphuric acid, and therefore in its formation from bromocamphoric anhydride as represented above, it is clear that the carboxyl group which is removed is also the *ortho*- one, or in other words lauronic acid contains the *allo*-carboxyl group of the original camphoric acid molecule.

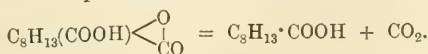
Taking the author's formula for camphoric acid as the basis, it will be seen at once that these changes are all easily understood, the following formulæ representing the constitution of the various substances mentioned above.



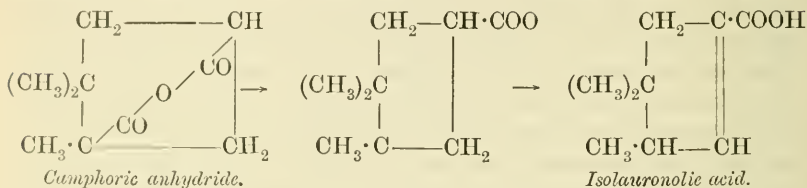
The formula for lauronic acid is in accordance with Walker's views, in so far that it represents this acid as a  $\beta\gamma$ -unsaturated acid, and thus accounts for the ease with which it is converted into campholactone on treatment with acid; and since *allo*-campholytic acid also readily yields campholactone with acids, it is very probable, as stated above, that it is stereoisomeric with lauronic acid.

In a similar manner, the constitution of *isolauronic acid* (and of *campholytic acid*) may be deduced from the author's camphoric acid

\* Lauronic acid is also produced in this decomposition



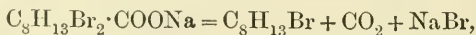
formula, either by considering the formation of this acid from sodium ethylic *ortho*-camphorate by electrolysis, or from camphoric anhydride by the action of aluminium chloride. In the latter case, the acid is formed simply by the elimination of CO from the *allo*-position, and thus leads to an intermediate formula, which, by necessary molecular re-arrangement, gives without difficulty the formula for isolauronolic acid.



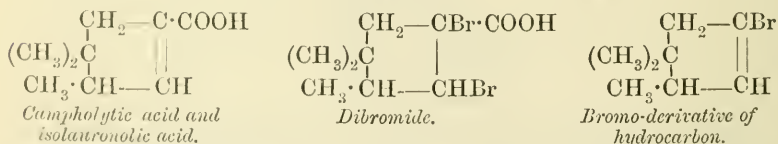
It will be noticed that the formula for isolauronolic acid given here is identical with that which was deduced for this acid on p. 810.

This formula appears to agree well with the known properties of isolauronolic acid; it represents the acid, for example, as an  $\alpha\beta$ -unsaturated acid, and thus accounts for the fact that it is not converted into a lactone on boiling with dilute acids.

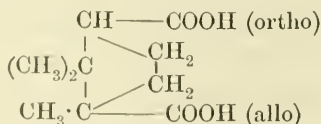
Isolauronolic acid is formed when campholytic acid is boiled with dilute acids, and it is therefore probable, as mentioned before, that these two acids are stereoisomeric. Now campholytic acid,  $\text{C}_9\text{H}_{14}\text{O}_2$ , yields a dibromide,  $\text{C}_9\text{H}_{14}\text{Br}_2\text{O}_2$ , which, when treated with sodium carbonate, gives a bromo-derivative of an unsaturated hydrocarbon (see p. 813),\*



and this kind of decomposition, which, as Fittig has shown, is confined to the dibrom-additive compounds of  $\alpha\beta$ -unsaturated acids, is very well understood with the aid of the above formula for campholytic acid.

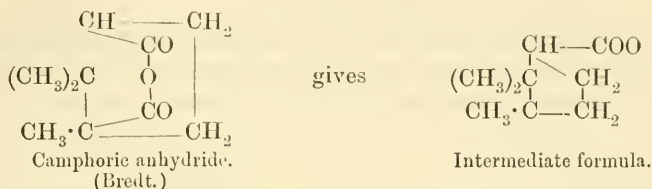


It may be easily shown that the formation and properties of lauronolic acid and isolauronolic acid, and the oxidation of the latter to isolauronic acid and dimethylacetylbutyric acid, cannot be satisfactorily explained with the aid of Bredt's formula for camphoric acid.

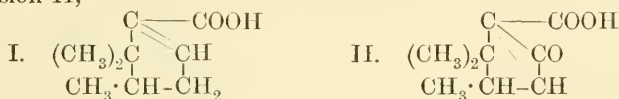


\* Isolauronolic acid seems to behave in the same way (Noyes, *Ber.*, 1895, **28**, 552).

If, in proof of this statement, we take the formation of isolaunonic acid by the action of aluminium chloride on camphoric anhydride, a reaction which, as was shown on p. 816, takes place with elimination of CO from the allo-position, we obtain the following result.

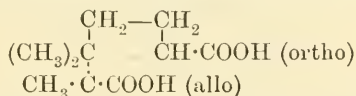


This intermediate formula must now undergo intramolecular change, and the only possible formula for isolaunonic acid which can be derived from this, and at the same time represent the acid as an  $\alpha\beta$ -unsaturated acid, is I, and if from this formula we now endeavour to deduce the constitution of isolaunonic acid,  $\text{C}_9\text{H}_{12}\text{O}_3$  (p. 806), we get the expression II,



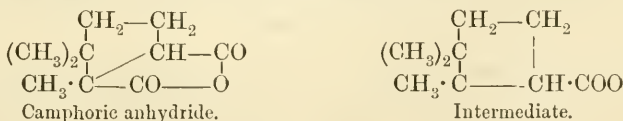
which does not account at all for the properties of this acid, and with the aid of which it seems quite impossible to imagine the formation of dimethylacetylbutyric acid,  $\text{CH}_3 \cdot \text{CO} \cdot \text{C}(\text{CH}_3)_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{COOH}$ , by further oxidation.

There is still one formula for camphoric acid which must be discussed, especially as it contains the group  $\begin{array}{c} \text{H} \quad \text{H} \\ | \quad | \\ -\text{C}-\text{C}-\text{COOH} \\ | \\ \text{C}-\text{COOH} \end{array}$ , which Walker (Trans., 1896, 59, 757), as the result of his investigations, considers must be present in this acid, and that is the formula.

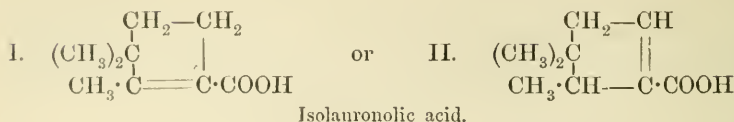


This formula was suggested by the author some time since (Proc., 1896, 191) as possibly being the correct expression for the constitution of camphoric acid.

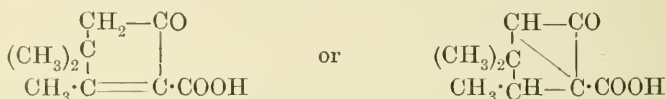
Using the same arguments as before, the formation of isolaunonic acid from this formula would be expressed thus.



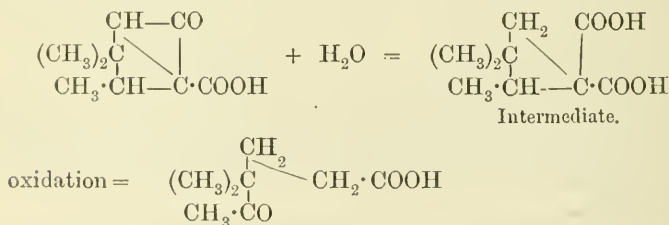




These views of the constitution of isolauronolic acid, although much more satisfactory than those derived from Bredt's formula, are nevertheless improbable, since they would lead to formulæ such as

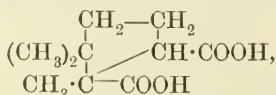


for isolauronic acid, which do not satisfy the condition 3 stated on p. 806. The first of these also could not give acetyldimethylbutyric acid on oxidation, and although the formation of this acid might be explained with the aid of the second formula, if it is assumed that the following changes could take place,



this assumption is highly improbable, since the intermediate trimethyltetramethylenedicarboxylic acid represented here would be a very stable substance, easily capable of isolation, and very difficult to attack by oxidising agents.

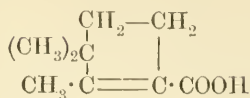
There are also other arguments against the formula,



for camphoric acid, such as, for example, the difficulty in explaining the lactone nature of camphanic acid, which appear to the author to make it much less probable than the formula adopted in this paper.

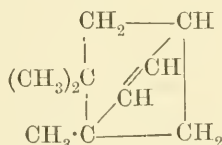
In a paper published a short time since (*Bull. Soc. Chim.*, 1898, [iii], 19, 534), G. Blanc starting with the formula\* given just above for camphoric acid, deduces the expression

\* This formula, which Blanc calls Bouveault's formula, for camphoric acid was first suggested by the author of this paper (*Proc.*, 1896, 191); Bouveault's communication did not appear till later (compare *Centralblatt*, 1897, ii, 856).



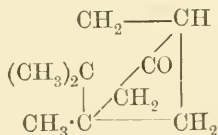
for isolaunonic acid, and states that this may be taken as “fixée avec la plus absolue certitude.” Blanc arrives at this formula (which is identical with that given on p. 818) from the consideration that, as isolaunonic acid is inactive, the asymmetry of the two asymmetric carbon atoms in camphoric acid must have disappeared in the formation of this acid, and he also explains that this formula readily accounts for the formation of acetyldimethylbutyric acid on oxidation.

The results of the examination of the ethylic and methylic salts of isolaunonic acid, which are given on p. 833, make it appear probable that this acid is feebly dextrorotatory,\* and in this respect it resembles borneocamphene, which is very feebly dextrorotatory. But, since borneocamphene gives camphoric acid on oxidation, it probably still contains *both* the asymmetric carbon atoms of the original camphor molecule, and its formula, on the basis of the camphor formula given on p. 798, may be represented as



It is well known that comparatively small changes in the structure of a substance often very much affect its rotation, and arguments as to constitution based on optical inactivity are useless until it is satisfactorily proved that the substance in question is really inactive and not merely a racemoid modification.

If the views expressed in this paper are correct, the constitution of camphor will be represented by the formula



which, as will be shown in a future paper, appears to account satisfactorily for the reactions of this substance.

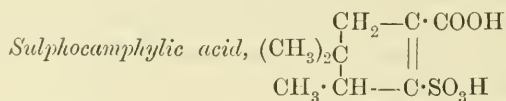
This research was commenced in 1889 in the laboratories of the Heriot Watt College, Edinburgh, and since 1892 it has been continued in the Owens College, Manchester. During the course of the

\* In order to decide this point, very careful experiments on the acid itself are in progress.

work, the author has received valuable assistance from Messrs. B. Prentice, W. H. Bentley, E. Haworth, J. L. Heinke, C. T. Abell, F. H. Lees, and others; he is also much indebted to Professors F. S. Kipping and James Walker for reading the manuscript and criticising the theoretical conclusions arrived at in the Introduction to this paper, and also to Prof. Ossian Aschan for valuable suggestions.

The author also wishes to state that the greater part of the heavy expense which is unavoidable in an investigation of this kind has been met by repeated Grants from the Research Fund of the Royal Society, without which it would hardly have been possible to have carried on these experiments.

#### EXPERIMENTAL.



In preparing small quantities of this acid, Koenigs and Hoerlein (*Ber.*, 1893, 26, 812) heated 20 grams of camphoric acid with 40 c.c. of sulphuric acid for 4—5 hours on a water bath, and after adding water and extracting the unchanged camphoric acid with ether, they evaporated to the crystallising point and purified the crude sulphocamphylic acid by recrystallisation from ethylic acetate. This process gives very good results, but it is not well adapted for preparing the acid in such quantities as were required for the present investigation; and after many experiments, the following method was devised, by which large quantities of sulphocamphylic acid may be obtained in an almost pure condition in a comparatively short time. Five hundred grams of camphoric acid\* and 1250 grams of concentrated sulphuric acid are heated in a large, round-bottomed flask on a briskly boiling water bath, when the crystals rapidly dissolve with evolution of much carbon monoxide, which must be carefully led away through a tube into the draught hole of a good draught cupboard, or, better still, into the open air. After 6—7 hours heating, the thick, brown liquid is left until cold, and then mixed with an equal volume of water, and allowed to stand overnight to crystallise, when the whole generally sets to a solid cake. The crystals, which consist of crude sulphocamphylic acid, are collected with the aid of the pump, and freed as far as possible from the dark mother liquors by pressure; these mother liquors were always discarded, as, although by suitable treatment an appreciable amount of

\* The whole of the camphoric acid used in this research was obtained from Kahlbaum, and it was always found to be of very excellent quality.



*Salts of Sulphocamphylic Acid.*

*Hydrogen Potassium Sulphocamphylate*,  $C_9H_{13}SO_5K + H_2O(?)$ .—This salt was prepared by dissolving sulphocamphylic acid in water, dividing the solution into two parts, neutralising the one with pure potassium carbonate, and then adding the other. It is readily soluble in water, and crystallises in magnificent tabular crystals which do not become opaque on exposure to the air, and do not lose weight at  $100^\circ$ . When dry, this salt has the appearance of alabaster, and breaks up into flakes on pounding in a mortar. Analysis.

0.4305 gram of the salt gave 0.1320  $K_2SO_4$ .  $K = 13.76$ .

$C_9H_{13}SO_5K + H_2O$  requires  $K = 13.45$ .

$C_9H_{13}SO_5K$  requires  $K = 14.33$ .

From the results of this analysis, it is possible that this salt crystallises with  $1H_2O$ .

*Potassium Sulphocamphylate*,  $C_9H_{12}SO_5K_2$ .—Considerable quantities of this salt were prepared during the experiments on sulphocamphylic chloride (p. 823) by exactly neutralising an aqueous solution of sulphocamphylic acid with potassium carbonate, and then concentrating on the water bath. The mass of colourless crystals which separated on standing was collected with the aid of the pump, rapidly washed with small quantities of water, and drained on a porous plate. The air dried salt does not appear to contain water of crystallisation, since the loss at  $150^\circ$  only amounted to 0.8 per cent.

0.4328, dried at  $150^\circ$ , gave 0.2493  $K_2SO_4$ ;  $K = 25.82$ .

$C_9H_{12}SO_5K_2$  requires  $K = 25.16$ .

This salt crystallises in small needles, and is very readily soluble in water.

*Hydrogen Sodium Salt*,  $C_9H_{13}SO_5Na + 5H_2O$ .—This salt was accidentally prepared during the course of some experiments on the action of sodium hydrogen sulphite on sulphocamphylic acid; a very strong solution of the acid was nearly neutralised with sodium carbonate, and then a saturated solution of sodium hydrogen sulphite was added. On standing, a quantity of iridescent plates separated, which were collected and purified by recrystallisation from water. The crystals, after being allowed to stand on a porous plate exposed to the air for 3 days, were analysed.

I. 0.5556 gram, heated at  $100^\circ$  for  $2\frac{1}{2}$  hours, lost 0.1156  $H_2O = 20.8$  per cent., and the residue, on treatment with sulphuric acid, gave 0.1196  $Na_2SO_4$ .  $Na = 6.98$  per cent.

II. 0.4490 gram, heated at  $100^\circ$  until constant, lost 0.0901  $H_2O =$



20·28 per cent. This salt very probably has the formula  $C_9H_{13}SO_5Na + 5H_2O$ , which contains 6·65 per cent. of sodium, and when heated at  $100^\circ$  it loses  $4H_2O$  or 20·81 per cent. of water.

Besides these salts, Koenigs and Hoerlin (*Ber.*, 1893, 26, 813) prepared and analysed the *neutral silver salt*,  $C_9H_{12}Ag_2SO_5 + 2H_2O$ , the *hydrogen silver salt*,  $C_9H_{13}AgSO_5 + 2H_2O$ , and a beautifully crystalline *hydrogen lead salt*,  $(C_9H_{13}SO_5)_2Pb + 6H_2O$ .

Carl Meyer (*Dissertation Munich*, 1895, p. 25) also prepared the *methylic salt*,  $C_9H_{12}SO_5(CH_3)_2$  (m. p.  $72^\circ$ ), and a *hydrogen methylic salt*,  $C_9H_{13}SO_5 \cdot CH_3$  (m. p.  $140^\circ$ ).

### *Sulphocamphylic Chloride*, $C_8H_{12}(COOH) \cdot SO_2Cl$ .

This substance is formed when dry potassium sulphocamphylate is treated with phosphorus pentachloride. When mixed under ordinary conditions, these two compounds reacted with considerable violence, much heat was developed, and the whole became converted into a carbonaceous mass from which nothing crystalline could be extracted, and for a long time all attempts to prepare sulphocamphylic chloride were unsuccessful.

Ultimately, however, by working at low temperatures, and mixing the substances in small portions at a time, so as to avoid, as far as possible, rise of temperature, it was found possible to isolate sulphocamphylic chloride in sufficient quantities to allow of its properties being carefully investigated. The method of preparation and extraction employed is as follows.

Phosphorus pentachloride (100 grams) is weighed out into a narrow beaker containing a thermometer, and cooled by a freezing mixture to at least  $-10^\circ$ , and carefully dried potassium sulphocamphylate (40 grams) is then gradually added in quantities of about 2 grams at a time, the whole being rapidly stirred with the thermometer after each addition, great care being taken during the operation that the temperature does not rise above  $0^\circ$ . When all the potassium salt has been added, the beaker is left in an ice chest overnight, and the dark brown, almost black, product is then stirred with powdered ice; after standing for about an hour, the dark, insoluble precipitate is collected, washed with water, and allowed to remain in contact with porous porcelain in a cool place until quite dry. The almost black product thus obtained is now ground up with sand, transferred to a Soxhlet apparatus, and extracted with dry ether, when the whole of the sulphochloride passes into the ether, leaving a large quantity of an insoluble, black residue. If the brown, ethereal solution is evaporated in a flask to a small bulk, and the flask loosely corked, and allowed to stand in an ice chest, crude sulphocamphylic chloride separates in brown crusts, which may

be obtained almost colourless by repeated recrystallisation from ether with the aid of animal charcoal.

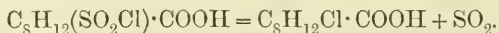
0.1994 gave 0.1124 AgCl.  $\text{Cl} = 13.93$ .

$\text{C}_8\text{H}_{12}(\text{COOH})\cdot\text{SO}_2\text{Cl}$  requires  $\text{Cl} = 14.05$  per cent.

Sulphocamphylic chloride melts at  $168^\circ$ , with decomposition. It is readily soluble in alcohol and warm acetic acid, but only sparingly in benzene and light petroleum, and crystallises beautifully either from dilute acetic acid or from dilute alcohol. It dissolves in cold sodium carbonate solution, and may be reprecipitated unchanged on the addition of acids; if, however, the alkaline solution is warmed for a few minutes, the sulphochloride is converted into sulphocamphylic acid, and no precipitation takes place on acidifying.

*Chlorodihydro- $\beta$ -camphylic Acid*,  $\text{C}_8\text{H}_{12}\text{Cl}\cdot\text{COOH}$ .

When strongly heated, sulphocamphylic chloride readily undergoes decomposition, with elimination of sulphur dioxide and formation of *chlorodihydro- $\beta$ -camphylic acid*, thus,



In investigating this decomposition, pure sulphocamphylic chloride, in quantities of about 10 grams, was heated under reduced pressure in a small retort connected with a long glass air condenser\* until the evolution of sulphur dioxide had ceased; on rapidly distilling the residue, almost the whole passed over at  $195\text{--}200^\circ$  (45 mm.) as a light greenish oil, which, on cooling, solidified completely. The solid distillate, which consisted of almost pure chlorodihydro- $\beta$ -camphylic acid, was dissolved in boiling light petroleum (b. p.  $50\text{--}60^\circ$ ), filtered, and the solution allowed to cool slowly, when beautiful, colourless needles were gradually deposited which, on analysis, gave the following numbers.

0.1354 gave 0.2852  $\text{CO}_2$  and 0.0870  $\text{H}_2\text{O}$ .  $\text{C} = 57.44$ ;  $\text{H} = 7.14$ .

0.2044 „ 0.1480 AgCl.  $\text{Cl} = 17.92$ .

0.2225 „ 0.1651 AgCl.  $\text{Cl} = 18.36$ .

$\text{C}_8\text{H}_{12}\text{Cl}\cdot\text{COOH}$  requires  $\text{C} = 57.32$ ;  $\text{H} = 6.9$ .  $\text{Cl} = 18.78$  per cent.

Chlorodihydro- $\beta$ -camphylic acid melts at  $105\text{--}106^\circ$ , and is readily soluble in alcohol, ether, chloroform, acetic acid, and warm light

\* In carrying out this operation, it is necessary to use a condenser at least 2 feet long, and to avoid, as far as possible, narrow openings in connecting the apparatus with the vacuum pump, as during the decomposition the chlorodihydro-camphylic acid is carried over by the sulphur dioxide to such an extent as to readily block up the connections and cause an explosion.

petroleum, but almost insoluble in water; it is best crystallised from light petroleum or from dilute acetic acid.

It dissolves in dilute sodium carbonate solution without decomposition, and the cold solution instantly decolorises permanganate, but the experiments on this oxidation hitherto made have not given very definite results. The solution of the acid in chloroform does not decolorise bromine, even on long standing, and the acid does not appear to react with hydrogen bromide at ordinary temperatures, since its solution in glacial acetic acid, after being saturated with hydrogen bromide and kept for some days, deposits the unchanged substance when evaporated over potash in a vacuum desiccator.

In chlorodihydro- $\beta$ -camphylic acid the chlorine is very firmly held, as is shown by the fact that, even if the solution of the acid in sodium carbonate is left in contact with excess of sodium amalgam, very little reduction takes place; if, however, the acid is boiled with sodium amalgam, reduction does take place, with formation of substances which are at present under investigation.

*Dibromo-chlorodihydro- $\beta$ -camphylic acid*,  $C_8H_{12}Br_2Cl \cdot COOH$ .

The action of bromine on chlorodihydro- $\beta$ -camphylic acid was investigated in order to show that this substance is unsaturated, and thus to obtain indirect evidence of the unsaturated nature of sulpho-camphylic acid. Bromine appears to have little action on the solution of chlorodihydrocamphylic acid in chloroform, and although the dry halogen reacts readily, a good deal of hydrogen bromide is evolved, and considerable difficulty was experienced in isolating the product. This was ultimately accomplished as follows. The finely powdered acid, in quantities of half a gram, was exposed on a watch-glass in a desiccator containing bromine and sulphuric acid for about  $1\frac{1}{2}$  hours, until the substance had become coloured red throughout by the bromine, care being taken to remove the watch-glass before the mass commenced to become liquid. The product was left exposed to the air until the excess of bromine had evaporated, and the sticky residue was then ground up in a mortar several times with small quantities of light petroleum (b. p.  $40-50^\circ$ ); about half of it dissolved, leaving a residue which was very sparingly soluble in light petroleum. This may be recrystallised from dilute alcohol if the operation is rapidly performed, and in this way beautiful, glistening prisms are obtained which gave the following results on analysis.

0.1656 gave 0.1910  $CO_2$  and 0.0576  $H_2O$ .  $C = 31.45$ ;  $H = 3.86$ .

$C_8H_{12}Br_2Cl \cdot COOH$  requires  $C = 30.99$ .  $H = 3.73$  per cent.

0.1342 gram gave 0.1995 gram of the mixed chloride and bromide of

silver, the amount required by the formula  $C_8H_{12}Br_2Cl \cdot COOH$  being 0.1994 gram.

Dibromochlorodihydro- $\beta$ -camphylic acid decomposes rapidly at about  $171-172^\circ$ . It is readily soluble in alcohol, benzene, chloroform, and acetic acid, almost insoluble in cold light petroleum, and, as stated above, it may be recrystallised from dilute alcohol if the operation be rapidly performed, otherwise the acid decomposes, with formation of a substance, not yet investigated, which melts at about  $100-102^\circ$  and decomposes with evolution of gas at  $150-160^\circ$ .

Dibromochlorodihydrocamphylic acid dissolves in dilute caustic soda, and the solution, on gently warming, rapidly deposits bromoform; if this be removed and the aqueous solution acidified, an oily acid separates which, on standing, gradually solidifies.

*$\beta$ -Camphylic Acid,  $C_8H_{11} \cdot COOH$ .*

This acid is formed when chlorodihydro- $\beta$ -camphylic acid is digested with alcoholic potash, hydrogen chloride being eliminated according to the equation



The pure acid was dissolved in a little alcohol, the solution heated to boiling in a reflux apparatus, and then a large excess of strong alcoholic potash added in small quantities at a time; decomposition takes place slowly, with separation of potassium chloride. After boiling for 2 hours, water was added, the solution evaporated until free from alcohol, cooled well, and acidified with hydrochloric acid, when an almost colourless, crystalline acid separated; this, after recrystallisation from dilute acetic acid, melted at  $103-105^\circ$ , and on examination proved to be  $\beta$ -camphylic acid.

0.1505 gave 0.3896  $CO_2$  and 0.1064  $H_2O$ .  $C = 70.60$ ;  $H = 7.85$ .

$C_8H_{11} \cdot COOH$  requires  $C = 71.05$ ;  $H = 7.89$  per cent.

$\beta$ -camphylic acid has been obtained in quantity by the fusion of sulphocamphylic acid with caustic soda, and a detailed description of the properties, and the discussion of the constitution of this interesting substance, is reserved for a future communication.

*Sulphocamphylic Bromide,  $C_8H_{12}(COOH) \cdot SO_2Br$ .*

This can be prepared by treating dry potassium sulphocamphylate with phosphorus pentabromide, the reaction being much less violent than is the case with phosphorus pentachloride (p. 823). The dry potassium salt (16 grams) is gradually mixed in a mortar with the pentabromide (60 grams), when a vigorous action sets in, torrents of



hydrogen bromide are evolved, and the mass becomes quite pasty. After standing for 2 hours, the product is stirred with powdered ice until the crude sulphobromide has become quite hard, the whole is then collected, and the ochre-coloured precipitate washed well with water, and dried on a porous plate at the ordinary temperature. The product is purified by recrystallisation from ether, exactly as in the case of the corresponding sulphochloride, and the sample employed for analysis was also recrystallised from dilute alcohol.

0.1598 gave 0.2120  $\text{CO}_2$  and 0.0603  $\text{H}_2\text{O}$ .  $\text{C} = 36.18$ ;  $\text{H} = 4.20$ .

0.1846 „ 0.1146  $\text{AgBr}$ .  $\text{Br} = 26.45$ .

$\text{C}_8\text{H}_{12}(\text{COOH})\text{SO}_2\text{Br}$  requires  $\text{C} = 36.36$ ;  $\text{H} = 4.37$ .  $\text{Br} = 26.93$  per cent.

When heated in a capillary tube, sulphocamphylic bromide softens at about  $147^\circ$  and melts at  $150^\circ$  with decomposition, due to elimination of sulphur dioxide. It is readily soluble in alcohol and in boiling benzene, but only sparingly in the latter solvent, and also in ether or light petroleum in the cold.

*Bromodihydro- $\beta$ -camphylic Acid*,  $\text{C}_8\text{H}_{12}\text{Br}\cdot\text{COOH}$ .

At temperatures slightly above its melting point, sulphocamphylic bromide decomposes rapidly with evolution of sulphur dioxide and formation of *bromodihydro- $\beta$ -camphylic acid*; but at the same time a quantity of carbonaceous matter is formed, and unless care is taken in carrying out the decomposition, it is almost impossible to extract the product and obtain it in a crystalline condition. The best results were obtained in the following way. Test tubes containing each about 2 grams of sulphocamphylic bromide were gradually heated in a sulphuric acid bath until the temperature reached  $155^\circ$ , when decomposition rapidly set in, with evolution of sulphur dioxide. After remaining for a few seconds at this point, the temperature was allowed to sink to about  $140^\circ$ , and kept at this until no more sulphur dioxide was evolved.

If the uninviting-looking, black, tarry product be now digested with light petroleum (b. p.  $60^\circ$ ) the brominated acid will be extracted, the tarry impurity remaining undissolved, and the yellow solution, on standing in flat basins at the ordinary temperature, deposits ochre-coloured, crystalline crusts as the solvent gradually evaporates.

The crude product was purified by recrystallisation from dilute formic acid, with the aid of animal charcoal, an operation which must be rapidly carried out, as prolonged boiling with the formic acid decomposes the substance.

The pale, ochre-coloured, crystalline precipitate, which separates



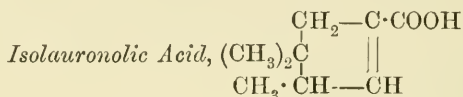
from the hot formic acid solution on rapidly cooling and stirring with a glass rod, gave the following results on analysis.

0.1518 gave 0.2580  $\text{CO}_2$  and 0.0775  $\text{H}_2\text{O}$ .  $\text{C} = 46.35$  ;  $\text{H} = 5.67$ .

0.2050 „ 0.1648  $\text{AgBr}$ .  $\text{Br} = 34.18$ .

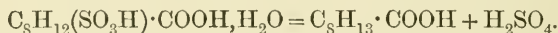
$\text{C}_8\text{H}_{12}\text{Br}\cdot\text{COOH}$  requires  $\text{C} = 46.34$  ;  $\text{H} = 5.57$  ;  $\text{Br} = 34.33$  per cent.

Bromodihydro- $\beta$ -camphylic acid melts at  $128\text{--}129^\circ$ , and when heated rapidly in small quantities, distils with very little decomposition. It dissolves readily in alcohol, benzene, acetic acid, and ether, but is only sparingly soluble in light petroleum. When digested with alcoholic potash, it behaves in the same way as chlorodihydro- $\beta$ -camphylic acid, yielding  $\beta$ -camphylic acid.



The isolauronolic acid required for this research was nearly all prepared by the two following methods.

I. *The Action of Heat on Sulphocamphylic Acid*.—When rapidly heated, crystallised, air dried sulphocamphylic acid is decomposed into isolauronolic acid and sulphuric acid, according to the equation



Unfortunately, at the temperature of the reaction the sulphuric acid formed decomposes much of the product, so that the yield of isolauronolic acid actually obtained is not more than 8—10 per cent. of the theoretical. The decomposition of sulphocamphylic acid was carried out under reduced pressure in small retorts connected by rubber joints with a long air condenser fitting into an ordinary distilling flask, the latter being connected with the water pump. On heating the sulphocamphylic acid (10 grams), the mass froths up without actually melting, and becomes black at a comparatively low temperature, white fumes coming over which partially condense in the condenser tube in beautiful, feathery groups like snow crystals, and partially pass over into the receiver in the form of an oil which rapidly solidifies. The distillation is stopped when oil ceases to come over ; and the retort, which is filled with a voluminous mass of carbon, is replaced by a fresh one. It was found best to distil the acid in quantities of not more than ten grams, as, if larger quantities are employed, the frothing, which is always most troublesome, becomes unmanageable.

The product, which smells strongly of sulphur dioxide and oil of turpentine, is dissolved in ether, the ethereal solution separated from

the water present, dried over calcium chloride, evaporated, and the solid residue, which contains oily impurity, allowed to remain in contact with porous porcelain until dry and nearly colourless. The crude isolauronolic acid thus obtained is then very easily purified by recrystallisation, either from dilute alcohol or from dilute acetic acid, from which solvents it separates in the form of beautiful, glistening prisms which melt at 133—135°. The analysis gave the following results.

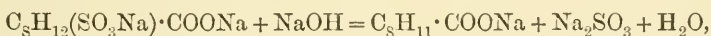
I. 0.1455 gave 0.3726  $\text{CO}_2$  and 0.1203  $\text{H}_2\text{O}$ .  $\text{C} = 69.89$  ;  $\text{H} = 9.18$ .

II. 0.1160 „ 0.2984  $\text{CO}_2$  „ 0.0961  $\text{H}_2\text{O}$ .  $\text{C} = 70.16$  ;  $\text{H} = 9.19$ .

$\text{C}_8\text{H}_{13}\cdot\text{COOH}$  requires  $\text{C} = 70.13$  ;  $\text{H} = 9.09$  per cent.

II. *Fusion of Sulphocamphylic Acid with Caustic Soda in Cast Iron Pots*.—When fused in cast iron vessels with caustic soda, sulphocamphylic acid undergoes a remarkable decomposition, yielding isolauronolic acid in considerable quantities, a reaction which, as explained in the introduction to this paper, evidently takes place in the following two stages.

In the first place, the sodium salts of  $\alpha$ - and  $\beta$ -camphylic acids\* are formed.



and these salts are then reduced by the iron of the cast iron vessel, with formation of the sodium salt of isolauronolic acid,



As this reaction was employed for preparing the greater portion of the isolauronolic acid used in this research, the following description of the process is given in detail.

Caustic soda (450 grams), mixed with about 250 c.c. of water in the outer vessel of an ordinary large glue-pot, is heated on a Fletcher ring burner until dissolved, and sulphocamphylic acid (150 grams) is added in small quantities at a time, and with constant stirring ; the temperature is then raised slowly to about 240°, and maintained at that point for 45 minutes. During this operation, pungent vapours are evolved, and with some practice the end of the reaction may be readily detected by the appearance of the melt, which becomes granular and nearly solid. The product, which is coloured dark reddish-brown by the ferric oxide which it contains, is dissolved out by hot water, and transferred to a large porcelain pot ; and when about 2 kilos. of sulphocamphylic acid have been fused in this way, the liquid is acidified and allowed to stand overnight, when the oil which separates will have become semi-solid.

\* A description of these interesting acids is reserved for a future communication.

This dark-brown, semi-solid mass is collected, washed with water, and stirred up with ether in large beakers until the organic matter is entirely dissolved; the ethereal solution is then decanted, filtered from the ferric oxide, dried over calcium chloride, and the ether distilled off. The oily residue, which usually weighs about 350 grams, is next twice fractionated under reduced pressure, when nearly the whole passes over between 170—190° (60 mm.) as a pale greenish oil, which on cooling solidifies completely. The crystalline cake is broken up and digested with excess of sodium carbonate and some animal charcoal, filtered, the filtrate acidified, and the crystalline precipitate collected and washed. In this way, a small quantity of a neutral substance smelling strongly of peppermint, and much colouring matter, is removed. In order to purify the crude isolauronolic acid thus obtained, it is dissolved in excess of ammonia, and submitted to distillation in steam, when the ammonium salt of isolauronolic acid dissociates, causing the acid to separate out in the flask, and to be partially carried over with the steam and ammonia. The distillate is acidified, and the precipitate, together with the acid which has separated in the flask, is collected, dissolved in sodium carbonate, heated on the water bath with purified animal charcoal for half an hour, and, after filtering, the acid is reprecipitated and purified by recrystallisation from dilute acetic acid or dilute alcohol, until the melting point rises to 133—135°. The analysis of three different preparations gave the following results.

0.1485 gave 0.3792 CO<sub>2</sub> and 0.1206 H<sub>2</sub>O. C = 69.61; H = 9.02.

0.1500 „ 0.3865 CO<sub>2</sub> „ 0.1235 H<sub>2</sub>O. C = 70.27; H = 9.28.

0.1489 „ 0.3826 CO<sub>2</sub> „ 0.1218 H<sub>2</sub>O. C = 70.05; H = 9.08.

C<sub>8</sub>H<sub>13</sub>.COOH requires C = 70.13; H = 9.09 per cent.

In preparing isolauronolic acid by this method, a quantity of oily impurity is removed from the crude crystals during the crystallisation from dilute acetic acid, and in order to investigate the nature of this, the mother liquors from a very large number of different preparations were mixed with water and extracted with ether. The ethereal solution was several times washed with water to remove the acetic acid, dried over calcium chloride, and evaporated; in this way, about 50 grams of a thick, yellow oil was obtained, which was carefully fractionated, first under reduced pressure, and then under ordinary pressure.

Rather more than 30 grams of the oil distilled between 230° and 245° (750 mm.), and this, on standing for some months in an ice chest, deposited a few crystals of isolauronolic acid. The oil was decanted from these crystals and again distilled, when nearly the whole passed over at 230—235° as a colourless oil, which on analysis gave the following results.

0.1436 gave 0.3548  $\text{CO}_2$  and 0.1236  $\text{H}_2\text{O}$ .  $\text{C} = 67.45$ ;  $\text{H} = 9.63$ .

0.1584 „ 0.3905  $\text{CO}_2$  „ 0.1391  $\text{H}_2\text{O}$ .  $\text{C} = 67.23$ ;  $\text{H} = 9.75$ .

$\text{C}_7\text{H}_{13}\cdot\text{COOH}$  requires  $\text{C} = 67.60$ ;  $\text{H} = 9.86$  per cent.

The silver salt of this acid was prepared by precipitating a slightly alkaline solution of the ammonium salt with silver nitrate; and the white, caseous precipitate was analysed, with the following results.

0.1943 gave 0.2693  $\text{CO}_2$ , 0.0860  $\text{H}_2\text{O}$ , and 0.0855  $\text{Ag}$ .

$\text{C} = 37.80$ ;  $\text{H} = 4.91$ ;  $\text{Ag} = 44.00$ .

$\text{C}_7\text{H}_{13}\cdot\text{COOAg}$  requires  $\text{C} = 38.55$ ;  $\text{H} = 5.22$ ;  $\text{Ag} = 43.38$  per cent.

From these results, it seems probable that this oil, boiling at  $230\text{--}235^\circ$ , is an acid of the composition  $\text{C}_7\text{H}_{13}\cdot\text{COOH}$ , but, as its examination did not give any results which seemed likely to be of value in the present inquiry, its systematic investigation was not undertaken.

*Properties and Salts of Isolauronolic Acid.*—Isolauronolic acid melts at  $133\text{--}135^\circ$ , and distils without decomposition at about  $250^\circ$  under the ordinary pressure; it is readily volatile in steam. It dissolves readily in alcohol, ether, chloroform, benzene, carbon bisulphide or ethylic acetate, but is only very sparingly soluble in water. The solution of the acid in sodium carbonate is oxidised by potassium permanganate instantly at the ordinary temperature, but bromine is not decolorised by the solution of the acid in chloroform except on warming or long standing, and then with evolution of hydrogen bromide. Isolauronolic acid is not readily attacked by hydrogen bromide, since it does not form an additive compound when its solution in glacial acetic acid is saturated with hydrogen bromide and allowed to stand overnight; this is shown to be the case by adding water to the solution, when the acid is reprecipitated unchanged.

Noyes (*Ber.*, 1895, 28, 552) succeeded in obtaining a dibromide of isolauronolic acid,  $\text{C}_8\text{H}_{13}\text{Br}_2\cdot\text{COOH}$ , melting at  $138\text{--}140^\circ$ , by treating the solution of the acid in dry chloroform with bromine, in the dark, at temperatures below  $0^\circ$ , and he has also prepared a crystalline hydrobromide,  $\text{C}_8\text{H}_{14}\text{Br}\cdot\text{COOH}$  (m. p.  $127\text{--}130^\circ$ ), which he obtained by shaking the acid with fuming aqueous hydrobromic acid and light petroleum.\* Isolauronolic acid is not reduced when treated with a large excess of sodium amalgam, but it yields a *dihydro-derivative*,  $\text{C}_8\text{H}_{15}\cdot\text{COOH}$ , when its solution in amyl alcohol is heated with sodium (see p. 836).

Isolauronolic acid does not form a lactone when boiled with dilute acids. This point has been very carefully investigated by heating

\* Private communication.



the acid with sulphuric acid of varying concentration and under various conditions, but in no case could a lactone be isolated.

The dissociation constant of isolauronolic acid has been determined by Walker (Trans., 1893, 63, 505) who found the very low value  $k = 0.0018$ .

Isolauronolic acid dissolves in dilute ammonia and in sodium hydrogen carbonate, but it is a very feeble acid, since its ammonium salt readily dissociates into ammonia and the free acid on evaporating its solution on the water bath. Koenigs and Hoerlin (Ber., 1893, 26, 814) state that the solution of the calcium salt of the acid is decomposed by carbon dioxide into calcium carbonate and the free acid, a decomposition seldom met with in organic calcium salts.

*Silver isolauronolate*,  $C_8H_{13} \cdot COOAg$ , was obtained, on adding silver nitrate to a neutral solution of the ammonium salt, as a white, caseous, and very voluminous precipitate which on analysis gave the following results.

I. 0.1967 gave 0.2976  $CO_2$ , 0.0884  $H_2O$ , and 0.0815 Ag.

C = 41.26 ; H = 4.99 ; Ag = 41.43.

II. 0.1625 gave 0.0672 Ag. Ag = 41.35.

$C_8H_{13} \cdot COOAg$  requires C = 41.38 ; H = 4.98 ; Ag = 41.38.

A neutral dilute solution of the ammonium salt of isolauronolic acid gives, with *copper sulphate*, a light blue, apparently crystalline, and very insoluble precipitate, and with *lead acetate* or *zinc sulphate*, a white, amorphous, caseous precipitate, but no precipitation with *barium* or *calcium chlorides*.

Koenigs and Hoerlin (*loc. cit.*) have prepared and analysed a *calcium salt* of isolauronolic acid,  $(C_9H_{13}O_2)_2Ca + H_2O$  (?),\* and the *potassium salt*,  $C_9H_{13}KO_2 + H_2O$ ; both of these salts are crystalline and soluble in water; according to Noyes (Ber., 1895, 28, 550), the calcium salt of isolauronolic acid crystallises with  $3\frac{1}{2}H_2O$ .

Walker (this Journal, 1893, 63, 506) has described the *barium salt* of isolauronolic acid as a soluble, crystalline substance, which appears to have the formula  $(C_9H_{13}O_2)_2Ba + 5H_2O$ .

*Ethereal Salts of Isolauronolic Acid.*—The methylic and ethylic salts of isolauronolic acid were prepared by dissolving the acid in the corresponding alcohol, adding concentrated sulphuric acid, allowing the mixture to stand for 12 hours, and then heating for 2 hours at 60–80°, etherification taking place very readily under these conditions. After adding water, the oily ethereal salts were extracted three times with ether, the ethereal solutions were well washed with water and dilute

\* The formula,  $C_9H_{13}CaO_2 + H_2O$ , given for this salt in Koenigs and Hoerlin's paper is obviously a slip.



sodium carbonate, dried over anhydrous potassium carbonate, and after distilling off the ether, the residue was purified by fractionation under the ordinary pressure. The determination of the densities, magnetic rotation, refraction, &c., of these ethereal salts was carried out by W. H. Perkin, sen.

*Methylic isolauronolate*,  $C_8H_{13} \cdot COOCH_3$ , a colourless liquid possessing a rather characteristic odour, boils at  $204-204.5^\circ$  without decomposition.

0.1114 gave 0.291  $CO_2$  and 0.0962  $H_2O$ . C = 71.24 ; H = 9.60.

$C_8H_{13} \cdot COOCH_3$  requires C = 71.43 ; H = 9.52 per cent.

The density determinations gave

$$\begin{array}{ll} d\ 4^\circ/4^\circ = 0.9835. & d\ 15^\circ/15^\circ = 0.9747. \\ d\ 10^\circ/10^\circ = 0.9784. & d\ 25^\circ/25^\circ = 0.9681. \end{array}$$

Prepared in the way described above, this methylic salt has a slight permanent rotation, which was found to be  $+7' 48''$  for a length of 10.2 cm. at  $30^\circ$ .

	<i>t</i> .	Sp. rotation.	Mol. rotation.
Magnetic rotation .....	$30^\circ$	1.1696	11.312
Refraction .....	$t = 17.3^\circ$ .	$d\ 17.3^\circ/4^\circ = 0.97207$ .	

	$\mu$ .	$\frac{\mu-1}{d}$ .	$\frac{\mu-1}{d} p$ .
A.....	1.46278	0.47607	79.981
Li .....	1.46575	0.47913	80.494
Ha .....	1.46634	0.47974	80.596
Na .....	1.46970	0.48319	81.176
H $\beta$ .....	1.47795	0.49168	82.603
H $\gamma$ .....	1.48517	0.49911	83.851

*Ethylic isolauronolate*,  $C_8H_{13} \cdot COOC_2H_5$ . B. p.  $216^\circ$ .

0.1170 gave 0.3112  $CO_2$  and 0.1049  $H_2O$ . C = 72.60 ; H = 9.96.

$C_8H_{13} \cdot COOC_2H_5$  requires C = 72.53 ; H = 9.89 per cent.

The density determinations gave

$$\begin{array}{lll} d\ 4^\circ/4^\circ = 0.9645. & d\ 10^\circ/10^\circ = 0.9596. & d\ 15^\circ/15^\circ = 0.9560. \\ d\ 20^\circ/20^\circ = 0.9527. & d\ 25^\circ/25^\circ = 0.9494. & \end{array}$$

This ethereal salt had a slight permanent rotation which was found to be  $+10' 12''$  for a length of 10.2 cm. at  $29^\circ$ .

	<i>t</i> .	Sp. rotation.	Mol. rotation.
Magnetic rotation.....	$28.5^\circ$	1.1623	12.405
Refraction .....	$t = 17.2^\circ$	$d\ 17.2^\circ/4^\circ = 0.95339$ .	

	$\mu$ .	$\frac{\mu-1}{d}$ .	$\frac{\mu-1}{d}p$ .
A .....	1.45950	0.48197	87.718
Li .....	1.46238	0.48498	88.267
H <sub>a</sub> ...	1.46307	0.48571	88.400
Na.....	1.46624	0.48903	89.004
H $\beta$ ...	1.47429	0.49748	90.541
H $\gamma$ ...	1.48127	0.50478	91.870

The results obtained in the examination of the magnetic rotation of methylic and ethylic isolauronolates are interesting. The difference in the values of the two ethereal salts is 1.093 and is normal, that is to say, it is the same as between the ethylic and methylic salts in the fatty series; thus, for example, the difference between the ethylic and methylic salts of butyric acid is 1.090.

Again, the values obtained afford important evidence that isolauronolic acid is an unsaturated acid, as the following comparison of ethylic isolauronolate with ethylic nonate shows. The magnetic rotation of ethylic nonate,  $C_8H_{17} \cdot COOC_2H_5$ , is 11.590, and assuming that ethylic isolauronolate is unsaturated, and at the same time a closed chain compound, its magnetic rotation may be approximately calculated.

From the examination of a large number of closed chain compounds, it has been found that these differ from the corresponding open chain saturated compounds by about  $-0.47$ , and also that unsaturated compounds have a higher rotation than the corresponding saturated compounds by about 1.112.

We have, therefore,

Magnetic rotation of ethylic nonate = 11.590

Add value for unsaturation = 1.112

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12.702

Deduct value for ring formation = 0.471

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Calculated magnetic rotation of ethylic isolauronolate = 12.231

The value thus calculated agrees well with that actually found, namely, 12.405.

The refractions of the methylic and ethylic salts of isolauronolic acid are very high, showing their unsaturated nature, as is evident from the following comparison between the values found and those calculated.

	Found.	Calculated.	Difference.
Methylic salt.....	80.596	77.0	+ 3.504
Ethylic salt .....	88.400	84.6	+ 3.800

*Methylic dibromisolauronolate*,  $C_8H_{13}Br_2 \cdot COOCH_3$ .—The action of

bromine on methylic isolauronolate was investigated in order to obtain further evidence as to the unsaturation of the acid. Methylic isolauronolate (3 grams) was dissolved in carefully dried chloroform (3 grams), and after cooling the solution to  $0^{\circ}$ , dry bromine (3 grams) dissolved in chloroform (10 grams) was slowly added, the apparatus being covered up so as to exclude light during the operation. The bromine was rapidly, but not instantaneously, absorbed, and as soon as the whole had been decolorised, the product, which, owing to the presence of traces of hydrogen bromide, fumed slightly, was freed from chloroform by passing a current of dry air through it for some hours. The thick oil thus obtained, after standing for some time over solid paraffin wax in a vacuum desiccator, gave the following results on analysis.

0.2171 gave 0.2994  $\text{CO}_2$  and 0.0931  $\text{H}_2\text{O}$ .  $\text{C} = 37.61$ ;  $\text{H} = 4.76$ .

0.1899 „ 0.2536  $\text{CO}_2$  „ 0.0772  $\text{H}_2\text{O}$ .  $\text{C} = 36.40$ ;  $\text{H} = 4.50$ .

0.3329 „ 0.3696  $\text{AgBr}$ ;  $\text{Br} = 47.24$ .

0.4172 „ 0.4650  $\text{AgBr}$ ;  $\text{Br} = 47.42$ .

$\text{C}_8\text{H}_{13}\text{Br}_2 \cdot \text{COOCH}_3$  requires  $\text{C} = 36.6$ ;  $\text{H} = 4.87$ ;  $\text{Br} = 48.77$ .

These results show that very little hydrogen bromide is eliminated when methylic isolauronolate is treated with the calculated quantity of bromine at  $0^{\circ}$  in the dark, since the product contains almost the quantity of bromine theoretically required for the dibrom-additive compound.

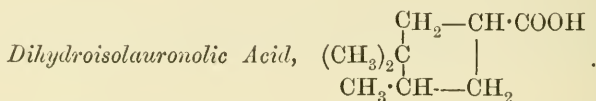
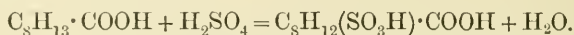
#### *Conversion of Isolauronolic Acid into Sulphocamphylic Acid.*

When isolauronolic acid, in quantities of 0.5 gram, is added to 10 times its weight of concentrated sulphuric acid, it dissolves with development of some heat, and formation of a yellow solution from which water precipitates the acid unchanged. If, however, the solution is gradually heated to  $75^{\circ}$ , it darkens and becomes brownish-black, a small amount of sulphur dioxide is liberated, and after heating some time no isolauronolic acid is deposited on adding water. After about 20 minutes heating at  $75^{\circ}$ , and as soon as a drop of the solution gave no precipitate on diluting with water, the well-cooled product was gradually mixed with an equal bulk of water, and the greenish solution left for some hours, when crystals separated; these were collected with the aid of the pump, dissolved in a little water, the solution warmed with animal charcoal, filtered, and evaporated nearly to dryness on the water bath. On standing in the ice chest, beautiful crystals of sulphocamphylic acid gradually formed; after draining these on a porous plate and subsequently drying at  $130^{\circ}$ , they gave the following results on analysis.

0.5547 gave 0.5451  $\text{BaSO}_4$ .  $S = 13.43$ .

$\text{C}_8\text{H}_{12}(\text{SO}_3\text{H})\cdot\text{COOH}$  requires  $S = 13.68$  per cent.

The careful examination of the properties of these crystals proved conclusively that they consisted of sulphocamphylic acid, and this acid, which is produced almost quantitatively in this way, is evidently formed from isolauronolic acid by the addition of sulphuric acid and elimination of water thus.



In the first experiments on the reduction of isolauronolic acid, it was treated with sodium amalgam under varied conditions, but no reduction took place even when its solution in sodium carbonate was boiled with a large excess of the amalgam; ultimately, it was found that the acid could be reduced, although with difficulty, when its solution in amylic alcohol was treated with sodium at the boiling temperature.

Pure isolauronolic acid (35 grams) was dissolved in isoamylic alcohol ( $1\frac{1}{2}$  litres), the solution heated to boiling on a sand bath in a flask connected with a long reflux condenser, and then 10 grams of sodium, in small pieces, was added all at once; as soon as the violent action had moderated somewhat, 20 grams more sodium was added, and the whole boiled vigorously until the sodium had dissolved. After allowing the mixture to cool, water was added, the product acidified with hydrochloric acid, the oily layer separated, and the aqueous liquid extracted twice with small quantities of isoamylic alcohol. The extract was then added to the main bulk, the whole distilled until the thermometer rose to  $125^\circ$ , when it was treated again with 30 grams of sodium exactly as in the first instance. After this process had been repeated three times, the product was extracted with water three times, the isoamylic alcohol distilled down to a small bulk, the remainder removed by distillation with steam, and the aqueous solution thus obtained added to the previous extracts. The whole was then heated on the water bath until quite free from isoamylic alcohol, acidified, and repeatedly extracted with ether; after drying over calcium chloride and evaporating off the ether, 35 grams of an almost colourless oil was obtained which, on standing for some days in an ice chest, deposited about 5 grams of unchanged isolauronolic acid. These crystals were removed by filtration, and the filtrate distilled; almost

the whole passed over at  $165^{\circ}$  (at 30 mm.) as a colourless oil which gave the following results on analysis.

0.1292 gave 0.3284  $\text{CO}_2$  and 0.1163  $\text{H}_2\text{O}$ .  $\text{C} = 69.27$ ;  $\text{H} = 10.00$ .

$\text{C}_8\text{H}_{15}\cdot\text{COOH}$  requires  $\text{C} = 69.23$ ;  $\text{H} = 10.25$  per cent.

Although this analysis agrees well with the numbers required by dihydroisolauronic acid, it was found that when a drop of the substance dissolved in dilute sodium carbonate was mixed with a trace of permanganate, the colour was instantly discharged, showing that it still contained some unchanged isolauronic acid, and since, for subsequent experiments, it was necessary that this should be removed, the following process of purification was resorted to.

The acid was dissolved in dilute sodium carbonate and oxidised by dilute permanganate in a vessel fitted with a turbine, the temperature being kept at  $0^{\circ}$  by means of powdered ice, and a rapid current of carbonic anhydride being passed during the whole operation. As soon as the pink colour remained permanent for several minutes, the excess of permanganate was destroyed by sodium hydrogen sulphite, the whole heated to boiling, filtered, and the filtrate and washings from the manganese precipitate evaporated to dryness. The residue was acidified, distilled in a current of steam,\* the oily acid extracted from the distillate in the usual way, and purified by distillation under reduced pressure, when nearly the whole passed over at  $144^{\circ}$  (22 mm.).

0.1272 gave 0.3221  $\text{CO}_2$  and 0.1168  $\text{H}_2\text{O}$ .  $\text{C} = 69.04$ ;  $\text{H} = 10.22$ .

$\text{C}_8\text{H}_{15}\cdot\text{COOH}$  requires  $\text{C} = 69.23$ ;  $\text{H} = 10.25$  per cent.

*Dihydroisolauronic acid* is a colourless, moderately mobile oil which smells like a high boiling fatty acid. It dissolves readily in sodium carbonate, and the solution of the sodium salt does not decolorise permanganate in the cold. The acid is, in fact, characterised by extraordinary stability, as even when boiled with permanganate it is only very slowly attacked, and all attempts to oxidise it with nitric acid were unsuccessful, since, after boiling it for a week with 50 per cent. nitric acid, more than 75 per cent. of the acid was recovered unchanged.

*Salts of Dihydroisolauronic Acid.*—The silver salt,  $\text{C}_8\text{H}_{15}\cdot\text{COOAg}$ , obtained as a white, gelatinous precipitate by adding silver nitrate to a slightly alkaline solution of the ammonium salt, was washed well with water and once with methylic alcohol.

0.2338 gave 0.0950 Ag.  $\text{Ag} = 40.64$ .

$\text{C}_8\text{H}_{15}\cdot\text{COOAg}$  requires  $\text{Ag} = 41.06$  per cent.

\* A considerable quantity of isolauronic acid separated from the residue in the distilling flask on standing.



This salt is very sparingly soluble in water, but it dissolves moderately readily in alcohol.

The *ammonium salt*, which separates in colourless crystals when the acid is mixed with moderately concentrated ammonia, is readily soluble in water, and dissociates when its solution is evaporated on the water bath. A slightly alkaline solution of the ammonium salt shows the following behaviour with reagents.

*Barium chloride*, no precipitate in the cold, but on boiling a crystalline barium salt separates, the crystals dissolving again on cooling.

*Calcium chloride* gives no precipitate with dilute solutions, but with moderately concentrated solutions a white calcium salt separates as an amorphous mass which becomes crystalline on warming.

*Copper acetate* gives at once a very pale blue, amorphous precipitate.

*Bromination of Dihydroisolaurenonic Acid, and its Reconversion into Isolaurenonic Acid.*

This experiment, which has such an important bearing on the constitution of isolaurenonic acid (p. 810), was conducted as follows.

Dihydroisolaurenonic acid (3 grams) was mixed in a reflux apparatus with phosphorus pentabromide (8 grams), and after the reaction, which commenced at once, had ceased, the mixture was heated for 10 minutes on the water bath. Bromine (3 grams) was then added to the well cooled product, and the whole very gently heated until the evolution of hydrogen bromide had practically ceased, and the colour of the bromine had disappeared.

The mixture of bromacid bromide and phosphorus oxybromide thus obtained was poured in a thin stream into excess of methylic alcohol; water was added, and the methylic salt, extracted with ether in the usual way, was washed with dilute sodium carbonate, dried, and fractionated under reduced pressure. Almost the whole of it (6 grams) distilled at 123—126° (30 mm.) as a colourless oil, and with liberation of traces of hydrogen bromide, which accounts for the analytical results being a little low.

0.3134 gave 0.2230 AgBr. Br = 30.27.

0.2904 „ 0.2050 AgBr. Br = 30.03.

$C_8H_{14}Br \cdot COOCH_3$  requires Br = 32.12 per cent.

When this *methylic bromodihydroisolaurenonolate* \* is mixed with warm alcoholic potash, a vigorous action takes place, accompanied by separation of potassium bromide, and if, after boiling for some minutes,

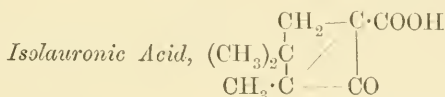
\* The free acid, called by Noyes  $\alpha$ -bromodihydro-*cis*-campholytic acid, is crystalline and melts at 124–125° (*Journ. Amer. Chem. Soc.*, 1896, 18, 689).

water is added and the alcohol removed by evaporation, a residue is obtained which, on acidifying, gives a crystalline precipitate; this, after being freed from traces of oily impurity by spreading it on porous porcelain, crystallises beautifully from dilute alcohol, and consists of pure isolaunonic acid (m. p. 133°).

0.1474 gave 0.1205  $\text{H}_2\text{O}$  and 0.3793  $\text{CO}_2$ .  $\text{C} = 70.18$ ;  $\text{H} = 9.08$ .

$\text{C}_8\text{H}_{13}\cdot\text{COOH}$  requires  $\text{C} = 70.13$ ;  $\text{H} = 9.09$  per cent.

The yield of isolaunonic acid obtained in this way appears to be almost quantitative.



This acid was first described by Koenigs and Meyer (*Ber.*, 1894, 27, 3467), who obtained it by oxidising isolaunonic acid with potassium permanganate at 0°.

Almost at the same time, and quite independently, the author carried out a series of experiments on the oxidation of isolaunonic acid, and after preparing a quantity of isolaunonic acid, carefully investigated it, with the result that many fresh facts were discovered which throw important light on the constitution both of this acid and of isolaunonic acid.

The isolaunonic acid used in these experiments was prepared as follows. Pure isolaunonic acid (5 grams) was dissolved in a slight excess of warm dilute potash, the solution transferred to a large porcelain beaker fitted with a turbine, and a rapid stream of carbon dioxide passed through the liquid. After adding powdered ice, and cooling the beaker externally by a freezing mixture, so that the temperature of the solution never exceeded  $-3^\circ$ , a well cooled saturated solution of potassium permanganate was slowly run in until the colour, which at first instantly disappeared, just remained permanent, the whole being stirred continuously, and a rapid current of carbon dioxide passed during the operation.\*

After the excess of permanganate had been destroyed by adding a little sodium hydrogen sulphite, the product was heated on the water bath, filtered from the manganese precipitate, and the filtrate, together with the washings of the precipitate, evaporated to a small bulk. On acidifying the deep yellow solution thus obtained, it deposited a mass of yellow crystals of isolaunonic acid,† which were collected with

\* If these precautions are not taken, the yield of isolaunonic acid is very much reduced.

† The mother liquors from these crystals contain considerable quantities of  $\gamma$ -dimethylacetylbutyric acid (see p. 844).

the aid of the pump, washed with water, and purified by recrystallisation from this solvent.

0.1730 gave 0.4069  $\text{CO}_2$  and 0.1141  $\text{H}_2\text{O}$ .  $\text{C} = 64.16$ ;  $\text{H} = 7.32$ .

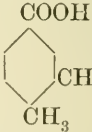
0.1557 „ 0.3667  $\text{CO}_2$  „ 0.1029  $\text{H}_2\text{O}$ .  $\text{C} = 64.22$ ;  $\text{H} = 7.34$ .

$\text{C}_9\text{H}_{12}\text{O}_3$  requires  $\text{C} = 64.22$ ;  $\text{H} = 7.14$  per cent.

*Isolauronic acid* crystallises from water in long, glistening, straw-yellow prisms and melts at  $133^\circ$ . It is readily soluble in hot water, ether, and alcohol, but only sparingly in light petroleum and cold water; it dissolves readily in sodium carbonate, and although the solution does not decolorise permanganate below  $0^\circ$ , it does so readily at the ordinary temperature. Isolauronic acid does not appear to form an additive compound with hydrogen bromide, since the solution of the acid in acetic acid saturated with hydrogen bromide, even on long standing, gives a precipitate of the unchanged acid on the addition of water. A solution of bromine in caustic potash oxidises the acid particularly easily on warming, with separation of bromoform and formation of an oily acid, which is at present under investigation.

Bromine vapour converts isolauronic acid into a red liquid, which gradually solidifies on standing over potash in a vacuum; the crystals, however, are very deliquescent, and as the substance could not be purified by recrystallisation from solvents, it was not further investigated.

When heated with concentrated aqueous hydrochloric acid at  $170^\circ$  for 3 hours, isolauronic acid is completely changed, with separation of a certain amount of carbonaceous matter. In order to find out what had been formed during this decomposition, the product was extracted with ether, the ethereal extract evaporated, the solid residue dissolved in sodium carbonate, and the solution, after boiling with animal charcoal and filtering, evaporated to a small bulk and acidified with hydrochloric acid. The almost colourless, sparingly soluble, sandy precipitate, which melted at  $165^\circ$ , after crystallisation from acetic

acid, was, on investigation, found to be paraxylic acid, , an

acid which Koenigs and Meyer (*Ber.*, 1894, 27, 3468) had already obtained from isolauronic acid by treatment with sulphuric acid.

*Salts of Isolauronic Acid.*—The silver salt,  $\text{C}_9\text{H}_{11}\text{AgO}_3$ , is obtained by adding silver nitrate to a warm neutral solution of the ammonium salt, as a colourless, crystalline precipitate, which dissolves moderately readily in hot water, and separates again on cooling as a beautiful, silky mass of crystals.

0.1732 gave 0.2492  $\text{CO}_2$ , 0.0642  $\text{H}_2\text{O}$  and 0.0684 Ag.

$\text{C} = 39.24$  ;  $\text{H} = 4.12$  ;  $\text{Ag} = 39.48$ .

$\text{C}_9\text{H}_{11}\text{AgO}_3$  requires  $\text{C} = 39.27$  ;  $\text{H} = 4.00$  ;  $\text{Ag} = 39.27$  per cent.

A dilute neutral solution of the ammonium salt of isolauronic acid gives no precipitate with *barium* or *calcium* chlorides even on boiling ; the addition of *copper* sulphate produces no precipitate in the cold, but on boiling a very pale blue, apparently crystalline, salt separates ; *lead* acetate gives at once a white, cascons precipitate which is soluble in hot water.

*Oxime of Isolauronic Acid*,  $\text{C}_7\text{H}_{11}(\text{C}:\text{NOH})\cdot\text{COOH}$ .—The action of hydroxylamine on isolauronic acid has been studied by Carl Meyer (*Dissertation Munich*, 1895, p. 39), who obtained in this way the oxime which he describes as a pale yellow powder which softens at  $215^\circ$  and decomposes at  $228\text{--}230^\circ$ . In preparing this substance in considerable quantities for experiments in connection with this research, the following method was always used. The pure acid (5 grams) was dissolved in moderately strong potash (15 grams), a solution of hydroxylamine hydrochloride (7 grams) added, and the whole after standing overnight was acidified, when the oxime was precipitated as a voluminous, amorphous precipitate somewhat resembling a precipitate of alumina. The whole was extracted 20 times with ether, and the ethereal solution, after being rapidly dried over calcium chloride, was evaporated until crystalline crusts of the oxime commenced to separate. After standing for some time, these were collected, washed with ether, and analysed.

0.1240 gave 8 c.c. of nitrogen at  $18^\circ$  and 762 mm.  $\text{N} = 7.47$ .

$\text{C}_9\text{H}_{13}\text{NO}_3$  requires  $\text{N} = 7.65$  per cent.

When heated in a capillary tube, the oxime of isolauronic acid turns brown at  $210^\circ$ , and melts with vigorous decomposition at  $222^\circ$ .

*Semicarbazone of Isolauronic Acid*,  $\text{C}_7\text{H}_{11}(\text{C}\cdot\text{N}_2\text{H}\cdot\text{CO}\cdot\text{NH}_2)\cdot\text{COOH}$ .—This very characteristic derivative is readily prepared by warming isolauronic acid with a slight excess of semicarbazide hydrochloride and sodium acetate on the water bath for a few minutes. The very sparingly soluble precipitate which separates rapidly on cooling was collected, washed with water, recrystallised from alcohol, and analysed, with the following result.\*

0.1444 gave 23.9 c.c. nitrogen at  $20^\circ$  and 740 mm.  $\text{N} = 18.42$ .

0.2178 „ 36.1 c.c. „  $18^\circ$  „ 745 mm.  $\text{N} = 18.70$ .

$\text{C}_{10}\text{H}_{15}\text{N}_3\text{O}_3$  requires  $\text{N} = 18.66$  per cent.

\* Carl Meyer (*Dissertation Munich*, 1895, p. 39), who has also prepared this semicarbazone, states that he always found 1 per cent. too much nitrogen in his analyses.

The *semicarbazone* of isolauronic acid melts at about 247—248° with decomposition.

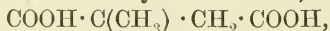
*Oxidation of Isolauronic Acid. Formation of  $\gamma$ -Dimethylacetylbutyric Acid,  $\text{CH}_3 \cdot \text{CO} \cdot \text{C}(\text{CH}_3)_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{COOH}$ , and  $\alpha$ -Dimethylsuccinic Acid,  $\text{COOH} \cdot \text{C}(\text{CH}_3)_2 \cdot \text{CH}_2 \cdot \text{COOH}$ .*

I.  *$\alpha$ -Dimethylsuccinic Acid.*—In the first experiments on the oxidation of isolauronic acid, 3 grams of the pure acid were dissolved in hot water, the solution heated to boiling in a reflux apparatus and then potassium dichromate and sulphuric acid run in through a tap funnel until very little further oxidation appeared to take place. The green solution, after saturating with ammonium sulphate, was extracted 10 times with ether, and the ethereal solution dried over calcium chloride and evaporated, when nearly 2 grams of a thick oil were obtained, which deposited crystals on standing; these were collected, drained on a porous plate, recrystallised from concentrated hydrochloric acid, and analysed, with the following result.

0.1520 gave 0.274  $\text{CO}_2$  and 0.0958  $\text{H}_2\text{O}$ .  $\text{C} = 49.15$ ;  $\text{H} = 7.0$ .

$\text{C}_6\text{H}_{10}\text{O}_4$  requires  $\text{C} = 49.31$ ;  $\text{H} = 6.85$  per cent.

This substance melted at 138—140°, and it seemed probable that it was identical with the  $\alpha$ -dimethylsuccinic acid,



which Leuckart (*Ber.*, 1885, 18, 2250) and Bischoff and Jaunsnicker (*Ber.*, 1890, 23, 3400) had obtained by the hydrolysis of the product of the action of ethylic  $\alpha$ -bromoisobutyrate on the sodium compound of ethylic malonate. In order to decide this point, the acid obtained from isolauronic acid was carefully compared with a sample of the synthetical acid which Professor Bischoff kindly sent the author, and in this way the identity of the two acids was clearly proved.

As it is a matter of importance, particularly for those working in the camphor group, to be able quickly to identify small quantities of  $\alpha$ -dimethylsuccinic acid, a short account of the more characteristic properties of this acid, together with a description of some new derivatives which were prepared during the above experiments, is given here.

$\alpha$ -Dimethylsuccinic acid is best purified by dissolving it in a little water, and saturating the well cooled solution with hydrogen chloride; on cooling, the acid rapidly separates in small crystals, which, after collecting on an asbestos filter, washing with hydrochloric acid, and draining on a porous plate, melt at 138—140°.

A characteristic of dimethylsuccinic acid, which is often very valuable in separating the acid from a mixture with other acids, is



the property that, when its aqueous solution is made strongly alkaline with ammonia and then mixed with excess of calcium chloride solution, no precipitate is formed in the cold, but on boiling a very sparingly soluble calcium salt separates, which, after collecting, washing with water, decomposing with hydrochloric acid and extracting with ether, yields at once the pure acid.\*

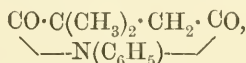
*α-Dimethylsuccinanilic acid* is readily prepared by heating the acid with excess of acetyl chloride for a few minutes, and after evaporating the excess of the chloride, dissolving the residue in benzene and adding aniline. In a short time, the anilic acid separates in crystals, which, after collecting and purifying by recrystallisation from dilute methylic alcohol, melt, when rapidly heated, at about 187° with rapid decomposition. The following analyses were made.

I. (From isolauroic acid) 0.1796 gave 9.8 c.c. of nitrogen at 16° and 755 mm. N = 6.32.

II. (From synthetical acid) 0.2695 gave 14.8 c.c. of nitrogen at 15° and 752 mm. N = 6.36.

$C_{12}H_{15}NO_3$  requires N = 6.33 per cent.

This anilic acid is readily decomposed by heating at 200—210°, with elimination of water and formation of *α-dimethylsuccinanil*,



a colourless, crystalline substance which, after recrystallisation from light petroleum (boiling point, 80—100°), melts at 87°. The following analyses were made.

I. (From isolauroic acid) 0.1801 gave 10.6 c.c. of nitrogen at 17° and 756 mm. N = 6.80.

II. (From synthetical acid) 0.2420 gave 14.9 c.c. of nitrogen at 15° and 760 mm. N = 7.21.

$C_{12}H_{13}NO_2$  requires N = 6.89 per cent.

\* This property has been made use of with great success in preparing *α*-dimethylsuccinic acid from the product of the action of ethylic *α*-bromisobutyrate on the sodium compound of ethylic malonate. When the product of this reaction is hydrolysed, a mixture of *α*-dimethylsuccinic acid and *α*-methylglutaric acid,  $\text{COOH} \cdot \text{CH}(\text{CH}_3) \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{COOH}$ , is obtained, and these two acids can only be separated with difficulty by crystallisation. If, however, the mixed acids are dissolved in excess of ammonia, calcium chloride added, and the clear solution heated to boiling, the whole of the calcium dimethylsuccinate is precipitated, whereas the calcium salt of methylglutaric acid remains in solution.

II. *γ*-Dimethylacetylbutyric Acid,  $\text{CH}_3 \cdot \text{CO} \cdot \text{C}(\text{CH}_3)_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{COOH}$ .

In oxidising isolauronic acid in the way just described, it was observed that the mother liquors from which the crude dimethylsuccinic acid had separated, and from which the last traces of this acid had been removed by calcium chloride, contained an oily acid which gave a precipitate of bromoform on treatment with bromine and caustic potash. In order to find out what this acid was, the oxidation was repeated under various conditions, but without result until ultimately the following process was devised.

Isolauronic acid (10 grams), in quantities of 1 gram, was oxidised on the water bath by means of potassium dichromate and sulphuric acid in such a way that, on cooling the solution, a small quantity of unchanged isolauronic acid always separated.\* The product from the 10 oxidations was left in an ice chest overnight, filtered from the long crystals of isolauronic acid which separated, the green solution evaporated at  $50^\circ$  to a small bulk, and extracted 10 times with pure ether. On evaporating the ether, a dark brown oil was obtained, which, although it was readily soluble in water, contained besides dimethylsuccinic acid and the new ketonic acid, also appreciable quantities of isolauronic acid. The whole was dissolved in a slight excess of ammonia, boiled with calcium chloride to precipitate the calcium dimethylsuccinate, filtered, acidified, and again repeatedly extracted with ether; after drying over calcium chloride, the ether was distilled off, and a light yellow, oily residue was left, which, even after standing for some weeks, did not show any signs of crystallising.

The crude oil was dissolved in water, mixed with a large excess of semicarbazide hydrochloride and the corresponding quantity of sodium acetate, and heated on a water bath at  $60^\circ$  for about 15 minutes, when a brownish semicarbazide rapidly separated, and on standing overnight a further quantity of a much paler coloured, crystalline precipitate was deposited. The whole was collected, washed with water, and boiled with a large quantity of water; about half the semicarbazide dissolved,† and on filtering while hot and allowing the filtrate to stand for some days, a brown, sandy precipitate gradually crystallised out. This was collected, purified by recrystallisation from large quantities of alcohol, and the colourless, crystalline precipitate thus obtained analysed, with the following results.

\* The isolauronic acid recovered from these oxidations crystallised from water in beautifully glistening needles which were nearly colourless, whereas this acid prepared as described in this paper, is always obtained in straw-yellow crystals; the yellow colour is therefore obviously due to impurity.

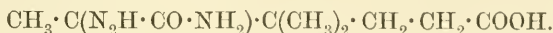
† The portion which remained undissolved was found on examination to consist of the semicarbazide of isolauronic acid.

0.1381 gave 0.2537 CO<sub>2</sub> and 0.0974 H<sub>2</sub>O. C = 50.07; H = 7.83.

0.1314 „ 22.4 c.c. nitrogen at 17° and 758 mm. N = 19.72.

C<sub>9</sub>H<sub>17</sub>N<sub>3</sub>O<sub>3</sub> requires C = 50.24; H = 7.9; N = 19.53 per cent.

The subsequent examination showed that this was the *semicarbazide* of  $\gamma$ -acetyldimethylbutyric acid,



$\gamma$ -Acetyldimethylbutyric acid was obtained from the semicarbazide by heating it on the water bath with dilute hydrochloric acid (1 vol. HCl to 2 vols. H<sub>2</sub>O) until the crystals had entirely dissolved, and then extracting the liquid repeatedly with pure ether. The ethereal solution, when dried over calcium chloride and evaporated, deposited a nearly colourless oil, which solidified when left over sulphuric acid for some days; on leaving the crystalline mass in contact with porous plates, the traces of oily impurity were completely absorbed, and colourless crystals were left, which, on analysis, gave the following results.

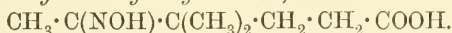
0.1572 gave 0.3487 CO<sub>2</sub> and 0.1236 H<sub>2</sub>O. C = 60.49; H = 8.73.

0.1415 „ 0.3145 CO<sub>2</sub> „ 0.1126 H<sub>2</sub>O. C = 60.62; H = 8.83.

CH<sub>3</sub> · CO · C(CH<sub>3</sub>)<sub>2</sub> · CH<sub>2</sub> · CH<sub>2</sub> · COOH requires C = 60.76; H = 8.86.

$\gamma$ -Acetyldimethylbutyric acid melts at about 50—51°, and is so readily soluble in organic solvents that it could not be satisfactorily recrystallised. This acid is identical with dimethyl-3-hexanon-2 acid, which Tiemann (*Ber.*, 1895, 28, 2176) prepared by the oxidation of  $\beta$ -dihydroxydihydrocampholenic acid with chromic acid mixture, and the melting point of which he found to be 48—49°.

*Oxime of  $\gamma$ -Acetyldimethylbutyric Acid,*



—In order to prepare this derivative, the acid (3 grams) was dissolved in dilute potash (4 grams), a strong solution of hydroxylamine hydrochloride (3 grams) added, and the whole allowed to stand overnight; on acidifying, a viscid mass separated, which, on shaking, rapidly solidified; this was collected, dried on a porous plate, purified by recrystallisation from hot water, and analysed.

0.1556 gave 0.3196 CO<sub>2</sub> and 0.1242 H<sub>2</sub>O. C = 56.01; H = 8.87.

0.2432 „ 18 c.c. of nitrogen at 20° and 760 mm. N = 8.46.

C<sub>8</sub>H<sub>15</sub>NO<sub>3</sub> requires C = 55.49; H = 8.67; N = 8.09 per cent.

This oxime is readily soluble in hot water, sparingly in cold water, and crystallises in long, colourless needles which melt at 97—98°.

*Reduction of  $\gamma$ -Acetyldimethylbutyric Acid. Formation of the Lactone of  $\gamma$ -Dimethyl- $\delta$ -hydroxycapronic Acid,*

$$\text{CH}_3 \cdot \underset{\text{O}}{\underset{|}{\text{CH}}} \cdot \text{C}(\text{CH}_3)_2 \cdot \text{CH}_2 \cdot \underset{\text{O}}{\underset{|}{\text{CH}_2}} \cdot \text{CO}$$

The reduction of acetyldimethylbutyric acid was investigated, as it was thought possible that the hydroxy-acid formed might be of value in connection with some synthetical experiments which are being carried out in the camphor series.

About 15 grams of the acid was dissolved in dilute sodium carbonate, and treated at the ordinary temperature with 500 grams of 3 per cent. sodium amalgam; after standing overnight, 200 grams more amalgam was added, and the whole heated on the water bath to complete the reduction. The alkaline solution, separated from the mercury, was acidified, saturated with ammonium sulphate, and extracted 10 times with ether; the ethereal solution was then dried with calcium chloride, evaporated, and the oily residue of hydroxy-acid submitted to fractional distillation. During this distillation, much water is eliminated, the thermometer then rises to  $235^\circ$ , almost the whole passing over between  $235^\circ$  and  $245^\circ$ , and, on again distilling, the lactone is easily obtained pure as a colourless oil possessing a faintly camphor-like odour, and boiling at  $239$ — $241^\circ$ .

I. 0.1235 gave 0.3074  $\text{CO}_2$  and 0.1056  $\text{H}_2\text{O}$ . C = 67.88; H = 9.50.

II. 0.1358 „ 0.3366  $\text{CO}_2$  „ 0.1189  $\text{H}_2\text{O}$ . C = 67.60; H = 9.72.

$\text{C}_8\text{H}_{14}\text{O}_2$  requires C = 67.60; H = 9.85 per cent.

The lactone of dimethylhydroxycapronic acid is isomeric with, and closely related to, the lactone of  $\gamma$ -ethyl- $\delta$ -hydroxycapronic acid,  $\text{CH}_3 \cdot \underset{\text{O}}{\underset{|}{\text{CH}}} \cdot \text{CH}(\text{C}_2\text{H}_5) \cdot \text{CH}_2 \cdot \underset{\text{O}}{\underset{|}{\text{CH}_2}} \cdot \text{CO}$ , which Fittig and Christ (*Annalen*, 1892, 268, 122) obtained by the reduction of  $\gamma$ -ethyl- $\gamma$ -acetylbutyric acid, and which boils at  $254$ — $255^\circ$ .

It is insoluble in water, and dissolves only very slowly on boiling with sodium carbonate solution. Caustic alkalis, however, readily dissolve it, with formation of the salts of the hydroxy-acid.

*Oxidation of Acetyldimethylbutyric Acid. Formation of  $\alpha$ -Dimethylglutaric Acid,*  $\text{COOH} \cdot \text{C}(\text{CH}_3)_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{COOH}$ .

When treated with bromine and caustic potash, acetyldimethylbutyric acid is readily oxidised, with separation of bromoform or tetrabromomethane, and formation of  $\alpha$ -dimethylglutaric acid.

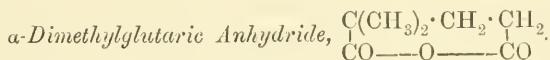
In investigating this decomposition, the pure acetyl acid was dissolved in a large excess of moderately concentrated aqueous potash,

the solution cooled to  $0^{\circ}$ , and bromine added, until, so far as could be seen, no further deposition of tetrabromomethane took place, and the solution, after standing for some minutes, was found to contain excess of hypobromite. After destroying the excess of hypobromite by passing sulphur dioxide into the solution, it was acidified with hydrochloric acid, saturated with ammonium sulphate, and extracted five times with pure ether; the ethereal solution, dried over calcium chloride, was then evaporated, when an oily residue was left, which, on standing in a vacuum over sulphuric acid, rapidly solidified.\* The crystalline mass was dissolved in a little water, and the well cooled solution saturated with hydrogen chloride, when, in a few hours, colourless, needle-shaped crystals separated; these, after draining on a porous plate and drying in a desiccator over potash and sulphuric acid, gave the following results on analysis.

I. 0.1408 gave 0.2701  $\text{CO}_2$  and 0.0956  $\text{H}_2\text{O}$ .  $\text{C} = 52.32$ ;  $\text{H} = 7.53$ .

II. 0.1126 „ 0.2168  $\text{CO}_2$  „ 0.0765  $\text{H}_2\text{O}$ .  $\text{C} = 52.51$ ;  $\text{H} = 7.62$ .  
 $\text{COOH} \cdot \text{C}(\text{CH}_3)_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{COOH}$  requires  $\text{C} = 52.50$ ;  $\text{H} = 7.50$  percent.

$\alpha$ -Dimethylglutaric acid melts at about  $84^{\circ}$ , and is readily soluble in water, alcohol, and most organic solvents, but only very sparingly in cold concentrated hydrochloric acid, separating from its hot solution in this solvent in woolly masses of fine needles. This acid has also been prepared by Tiemann (*Ber.*, 1895, 28, 2176), who showed that, when oxidised by nitric acid, it yields  $\alpha$ -dimethylsuccinic acid,  $\text{COOH} \cdot \text{C}(\text{CH}_3)_2 \cdot \text{CH}_2 \cdot \text{COOH}$ .

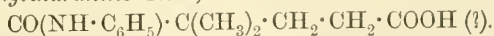


This was prepared by digesting the pure acid with excess of acetic anhydride for half an hour, and allowing the solution to evaporate over potash in a vacuum desiccator, when a colourless, syrupy residue was obtained, which soon solidified on being rubbed with a glass rod. The crystalline mass, after draining on a porous plate, melted at  $38^{\circ}$ , and consisted of  $\alpha$ -dimethylglutaric anhydride, as the following analysis shows.

0.1088 gave 2365  $\text{CO}_2$  and 0.0698  $\text{H}_2\text{O}$ .  $\text{C} = 59.27$ ;  $\text{H} = 7.13$ .

$\text{C}_7\text{H}_{10}\text{O}_3$  requires  $\text{C} = 59.15$ ;  $\text{H} = 7.04$  per cent.

$\alpha$ -Dimethylglutaranilic Acid,



—When a solution of dimethylglutaric anhydride in pure benzene is

\* If the oil does not solidify rapidly, the treatment with potash and bromine must be repeated.



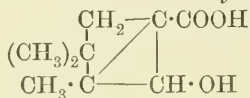
mixed with the calculated quantity of aniline, the corresponding anilic acid rapidly separates in crystals. These were collected, drained on a porous plate, and purified by recrystallisation from dilute alcohol, from which the substance separates in lustrous plates melting at  $144^{\circ}$  without decomposition.

0.2205 gave 11.5 c.c. of nitrogen at  $16.5^{\circ}$  and 768 mm.  $N = 6.07$ .

$C_{13}H_{17}NO_3$  requires  $N = 5.96$  per cent.

$\alpha$ -Dimethylglutaranilic acid is readily soluble in alcohol, but only sparingly so in water, benzene, or light petroleum.

*Reduction of Isolauronic Acid. Formation of Dihydroisolauronic Acid,*



The reduction of isolauronic acid was first studied by Carl Meyer (*Dissertation Munich*, 1895, p. 45), who treated the solution of the acid (1 gram) in sodium carbonate at ordinary temperatures with 40–50 grams of 3 per cent. sodium amalgam, a slow current of carbon dioxide being passed during the operation. After 24 hours, he acidified the product, digested it with dilute sulphuric acid for 1 hour, and then extracted with ether; the ethereal solution, after shaking with sodium carbonate to remove an acid (which is mentioned below) and evaporating off the ether, deposited a crystalline lactone,  $C_9H_{14}O_2$ , which melted at  $47\text{--}50^{\circ}$ , and gave on hydrolysis a hydroxy-acid melting at  $143^{\circ}$ ; it had, in fact, as mentioned in the Introduction, the properties of campholactone. On acidifying the soda solution from which the lactone had been extracted with ether, Carl Meyer obtained an oily acid which gradually solidified; this crystallised from light petroleum in nodular masses, and melted at  $80\text{--}81^{\circ}$ , the melting point not being altered by repeated crystallisation from light petroleum.

The analysis of this substance gave numbers which Carl Meyer thought indicated that it was a mixture of two acids,  $C_9H_{14}O_3$  and  $C_9H_{16}O_3$ .

Found, as a mean of four analyses,  $C = 62.95$ ;  $H = 8.66$  per cent.

$C_9H_{14}O_3$  requires  $C = 63.53$ ;  $H = 8.23$  per cent.

$C_9H_{16}O_3$      "      $C = 62.71$ ;  $H = 9.30$      "

This acid was not further reduced on treatment with sodium amalgam for several hours on the water bath; and, although no experiment seems to have been made with the object of determining whether it

was capable of forming a lactone, its method of isolation would seem to show that this is not the case.

In assigning the relative positions of the CO and COOH groups in isolauronic acid, it is obvious that it is a matter of the greatest importance to determine whether the acid formed by reducing this ketonic acid is capable of forming a lactone, and, for this reason, a very large number of experiments were instituted on the reduction of isolauronic acid under varied conditions. In the first place, Carl Meyer's experiment was repeated several times exactly as he described it, and using very pure isolauronic acid; but no trace of lactone could be obtained, and the hydroxy-acid, after extraction with ether and evaporating the solvent, solidified at once, and crystallised from light petroleum (b. p. 40—45°) in colourless leaflets which soften at 84—85° and melt at 88—89°.

The analysis gave numbers agreeing sharply with the formula  $C_9H_{14}O_3 = C_7H_{11}(CH \cdot OH) \cdot COOH$ .

0.1478 gave 0.3429  $CO_2$  and 0.1090  $H_2O$ . C = 63.27; H = 8.19.

0.1332 „ 0.3099  $CO_2$  „, 0.0985  $H_2O$ . C = 63.45; H = 8.22.

$C_9H_{14}O_3$  requires C = 63.53; H = 8.23 per cent.

This acid, for which the name *dihydroisolauronic acid* is proposed, was formed in all the experiments on the reduction of isolauronic acid, even when very varying conditions of temperature, concentration of solution, and quantities of reagents were employed, and it was the only product of reduction which the author could isolate. Dihydroisolauronic acid is moderately easily soluble in hot water, and crystallises from it, under certain conditions, in beautiful, colourless, glistening, prismatic needles which melt at 88—89°; it is very readily soluble in most organic solvents, and crystallises fairly well from light petroleum.

The solution of dihydroisolauronic acid in dilute sodium carbonate does not decolorise permanganate, except on long standing, and since it does not react with hydrobromic acid at the ordinary temperature, and its solution in chloroform does not decolorise bromine, it appears to be a saturated acid; this is confirmed by the fact, noticed by Carl Meyer, that the acid is not further reduced by sodium amalgam, even at 100°.

Dihydroisolauronic acid dissolves in concentrated sulphuric acid at 30°, forming a yellow solution, and at 40—50° decomposition sets in, with evolution of sulphur dioxide. If, after heating for a few minutes on the boiling water bath, the dark-coloured solution is poured into water, a yellow precipitate separates, which, on recrystallisation from acetic acid, melts at 164—165° and shows all the properties of paraxylic acid.

*Attempts to Convert Dihydroiselauronic Acid into a Lactone.*

For reasons stated in the Introduction to this paper, it was most important to determine whether dihydroiselauronic acid was capable of forming a lactone, and many experiments were made to decide this point.

I. In three experiments, the pure acid was digested with sulphuric acid of 10, 15, and 20 per cent. for 1 hour. The products from the first two experiments were extracted with ether, and the ethereal solution, after treatment with sodium carbonate, evaporated, but no trace of a lactone was obtained in either case, and on acidifying the sodium carbonate solution, the hydroxy-acid was recovered unchanged.

In the third experiment, in which 20 per cent. sulphuric acid had been used, the solution, on standing overnight, became filled with beautiful, glistening plates which melted at  $87^{\circ}$  with slight previous softening, and on examination were found to consist of the unchanged hydroxy-acid.

II. Dihydroiselauronic acid was heated in a sealed tube with water at  $220^{\circ}$  for 3 hours. On opening the tube, there was no pressure, and the light yellow oil which had separated below the water, on being touched with a crystal of the acid, solidified at once, and the crystals, after spreading on a porous plate, melted at  $85-87^{\circ}$ .

III. When heated in small quantities in a test-tube, dihydroiselauronic acid distils at a high temperature and condenses on the cooler portion of the tube as an oil which rapidly solidifies; the crystals, after being freed from traces of impurity by spreading on a porous plate, melt at  $80-85^{\circ}$  and consist of the unchanged acid, showing that the hydroxy-acid undergoes very little decomposition when distilled under the ordinary pressure. In order to clearly prove that dihydroiselauronic acid does not yield a lactone on heating, about 5 grams of the carefully dried acid was slowly distilled under reduced pressure (65 mm.); no elimination of water was observed, and the thermometer at once rose to  $215^{\circ}$ , the whole passing over between this temperature and  $220^{\circ}$  as a colourless oil which, on touching with a crystal of the original acid, immediately and completely solidified. This distilled acid, without further purification, gave the following results on analysis.

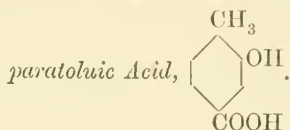
0.1771 gave 0.4152  $\text{CO}_2$  and 0.1341  $\text{H}_2\text{O}$ .  $\text{C} = 63.93$ ;  $\text{H} = 8.42$ .

Dihydroiselauronic acid,  $\text{C}_9\text{H}_{14}\text{O}_3$ , requires  $\text{C} = 63.53$ ;  $\text{H} = 8.23$  per cent.

This distilled acid melted at about  $78-84^{\circ}$ , dissolved completely in dilute sodium carbonate solution, and, as the analysis shows, consisted of unchanged dihydroiselauronic acid.

These experiments appear to the author to prove conclusively that *dihydroisolauroic acid is incapable of forming a lactone*.

*Fusion of Isolauroic Acid with Potash. Formation of Hydroxy-*



The behaviour of isolauroic acid on fusion with potash was investigated, because it was thought probable that in this way a more direct product of hydrolysis and oxidation might be obtained than had been found possible by submitting it to oxidation alone.

It was conceivable, for example, that the reaction might take the following course.



Isolauroic acid (1 gram) was dissolved in strong aqueous potash (10 grams), and the solution, which, on warming, rapidly became dark brown, was gradually heated at 130—140° until the frothing had subsided; the temperature was then raised to 230° for 10 minutes.

On acidifying, a milky solution smelling strongly of isobutyric acid was obtained, and on shaking it, a dark, resinous mass separated; this was extracted five times with ether, the ethereal solution evaporated, and the residue, which on standing overnight partially solidified, boiled with about 200 c.c. of water and filtered. The filtrate, decolorised by boiling with purified animal charcoal, was evaporated to a small bulk on the water bath, and on standing it deposited glistening plates, which were collected, recrystallised twice from water, and analysed, with the following result.

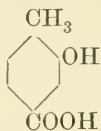
0.1291 gave 0.2978 CO<sub>2</sub> and 0.0642 H<sub>2</sub>O. C = 62.91; H = 5.52.

C<sub>8</sub>H<sub>8</sub>O<sub>3</sub> requires C = 63.15; H = 5.26 per cent.

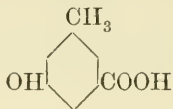
This acid melts at about 203—205° without decomposition, and when cautiously heated sublimes in feathery crystals; it dissolves readily in warm, sparingly in cold water, and crystallises from the hot solution, on slowly cooling, in beautiful, colourless, glistening prisms. When heated with acetic anhydride, it yields an acetyl compound, which crystallises from dilute alcohol in colourless needles and melts at 163—164°, but the amount obtained was too small for analysis.

As the results of the analysis and general properties of the acid clearly showed that it must be an aromatic compound, a search was

made among known hydroxy-acids of this composition, when two acids of similar properties were found, namely,



2-Hydroxyparatoluic acid,  
m. p. 206—207°.



5-Hydroxymetatoluic acid,  
m. p. 208.

Mr. J. L. Rose, B.Sc., a student of Owens College, kindly prepared for me a specimen of the former of these acids, using the method described by Weinreich (*Ber.*, 1887, 20, 981), which consists in sulphonating paratoluic acid and fusing the sulphonic acid with potash. The acid thus obtained, which melted at 206—207°, was digested with acetic anhydride for 1 hour, and when cold mixed with water and allowed to stand until it had completely solidified; this acetate, when purified by recrystallisation from benzene, separated in beautiful, colourless needles which melted at 162°, and gave the following result on analysis.

Found C = 61.99; H = 5.19.

$\text{CH}_3 \cdot \text{C}_6\text{H}_3(\text{O} \cdot \text{C}_2\text{H}_3\text{O}) \cdot \text{COOH}$  requires C = 61.85; H = 5.16 per cent.

The properties of the acid obtained by fusing isolauroic acid with potash agree, so far as they have been investigated, with those of hydroxyparatoluic acid, but as it is still possible that the acid may be hydroxymetatoluic acid, a specimen of the latter acid is being prepared in order that this point may be decided.

## LXXXV.—*Researches on the Terpenes. VIII. On Carvenol: its Reactions and Products.*

By JAMES E. MARSH and ALFRED HARTRIDGE.

In a paper published in the Transactions, 1897, p. 290, one of us, in conjunction with Mr. J. A. Gardner, described the production of an isomeride of camphor produced by the action of strong sulphuric acid on chlorocamphene. Subsequently, in a note in the Proceedings, we showed that the same substance was produced by the action of strong sulphuric acid on the isomeric chlorocamphene hydrochloride or so-called camphor chloride, obtained by the action of phosphorus pentachloride on camphor. The properties of this isomeride of camphor led us to regard it as a tertiary alcohol, and inasmuch as it was obtained



from chlorocamphene by displacing the chlorine by hydroxyl, we called it hydroxycamphene or camphenol, regarding it as a substitution derivative of camphene. In the present paper, we describe further experiments with this substance and the products obtained from it, and as we shall show that it is not a true substitution derivative of camphene, we must abandon the names hydroxycamphene and "camphenol." Moreover, we find we have no right to the name camphenol, as it has already been applied by Bouchardat and Lafont to certain isomerides of borneol which they have discovered. We propose, therefore, to call the substance carvenol, on account of the close relationship we find it to bear to carvacrol.

*Preparation and Purification of Carvenol.*—In order to prepare pure carvenol, we find it best to employ chlorocamphene obtained from  $\alpha$ -camphene dichloride by the process which has already been described (*loc. cit.*). As, however, the separation of the isomeric dichlorides is somewhat tedious, we employ, in preparing large quantities of the substance, the crude product of the action of phosphorus pentachloride on camphor. This is converted into chlorocamphene first by distilling the mixed chlorides, and subsequently by boiling the distilled product with aniline; the chlorocamphene is then dissolved in sulphuric acid containing 5 per cent. of water in the manner already described in the former paper, the action taking place in the cold, but being much accelerated by heating on the water bath. On pouring the clear solution into a large excess of water, the carvenol separates as a light yellowish liquid; by distilling this with steam, it is separated from a small quantity of tarry matter. The crude carvenol so obtained contains traces of chlorine, due to the presence in it, as will be shown later, of a small quantity of chlorocymene. To free it from this, it is again dissolved in sulphuric acid, and the solution shaken with light petroleum to remove the chlorocymene, which is insoluble in sulphuric acid. On now pouring the sulphuric acid solution into water, the substance is obtained free from chlorine, and is further purified by distillation under diminished pressure. Carvenol prepared from the crude product of the action of pentachloride of phosphorus on camphor is apt to contain some of the latter, which has escaped the action of the phosphorus pentachloride. This camphor comes over in the first fractions in the distillation of carvenol. We have found, however, that camphor is readily soluble in about its own weight of fuming hydrochloric acid of sp. gr. 1.2, whilst the camphene dichlorides are insoluble in it; this affords a ready method of removing the camphor from the crude camphene dichlorides.

The properties of carvenol have been described in the above-mentioned paper by Marsh and Gardner, and it was shown to be an isomeride of camphor. The specific gravity of a pure specimen free

from chlorine, and distilling at  $104^{\circ}$  under 10 mm. pressure, has been determined, and the density found to be  $d$  0.9372 at  $19.5^{\circ}/4^{\circ}$ . We have made further experiments with a view of ascertaining the nature of this substance.

*Action of Phosphorus Pentachloride on Carvenol.*—From the mode of formation of carvenol, it appeared probable that the chlorine of chlorocamphene was replaced by hydroxyl,  $C_{10}H_{15}Cl + H_2O = C_{10}H_{15}OH + HCl$ , so that we at first considered the substance to be a hydroxyl derivative of camphene; if this were so, we should expect that by the action of phosphorus pentachloride on carvenol we should get back the original chlorocamphene. This, however, is not the case. Pentachloride of phosphorus readily acts on carvenol, but it gives, not chlorocamphene, but chlorocymene,  $C_{10}H_{13}Cl$  [ $CH_3:Cl:C_3H_7 = 1:2:4$ ]. To prepare this substance, the carvenol is mixed with rather more than the theoretical amount of phosphorus pentachloride in a mortar, when hydrogen chloride is given off and the mass becomes liquid. It is then mixed with ice, and the oily liquid left undissolved is taken up with ether; the ethereal solution is shaken with a solution of sodium carbonate to remove a small quantity of an acid that is present, probably a phosphonic acid, which gives a crystalline sodium salt. The chlorocymene, which is the chief product, is obtained on distilling the ethereal solution, and can be further purified by shaking up with strong sulphuric acid, which removes impurities such as unaltered carvenol, whilst it has little or no action on chlorocymene in the cold. Chlorocymene obtained in this way boils at  $216^{\circ}$  under atmospheric pressure, and at  $103$ — $105^{\circ}$  under 19 mm.; it is a colourless liquid, and has no action on a cold solution of potassium permanganate. On analysis, it gave the following figures.

	Carbon.	Hydrogen.	Chlorine.
Found .....	71.5	7.9	20.9
Calculated for $C_{10}H_{13}Cl$	71.2	7.7	21.0

*Oxidation of Chlorocymene.*—Kekulé and Fleischer (*Ber.*, 1873, 6, 1087) obtained a chlorocymene by the action of phosphorus pentachloride on carvacrol, and found that, on oxidation, it gave a chlorotoluic acid melting at  $184$ — $186^{\circ}$ , but von Gerichten (*Ber.*, 1878, 11, 366) found the melting point to be  $199$ — $201^{\circ}$ . There is no doubt that our chlorocymene is identical with that of Kekulé and Fleischer, as it gives the same chlorotoluic acid on oxidation with nitric acid. (Kekulé and Fleischer do not state what oxidising agent they employed.) Claus and Davidson (*J. pr. Chem.*, [ii], 39, 497) have also obtained this acid from chlorotoluidine [ $Me:Cl:NH_2 = 1:2:4$ ] by Sandmeyer's reaction.

We find that on heating chlorocymene with nitric acid of sp. gr. 1.3

for about 24 hours on the water bath, it is practically entirely converted into a crystalline acid soluble in alcohol, and, when crystallised, from alcohol melting at 199°.

	Found.	Calc. $C_8H_7ClO_2$ .
Chlorine .....	20·3 per cent.	20·8 per cent.

*Chlorocymenesulphonic Acid*.—Chlorocymene, if left for a few hours in contact with strong sulphuric acid, gradually forms white crystals which do not dissolve readily in the acid; the action is aided by heating on the water bath. When 5 c.c. of chlorocymene was heated with 5 c.c. of strong sulphuric acid on the water bath, the mixture became solid after a time from the formation of crystals. These crystals were dissolved in water, and the boiling solution neutralised with barium carbonate, and filtered; on cooling, the barium salt crystallised out in long needles. It was analysed for water of crystallisation and for barium.

	Water at 120°.	Barium.
Found.....	14·49 per cent.	18·4 per cent.
Calculated .....	14·5 „	18·5 „

This agrees with the formula,  $Ba(C_{10}H_{12}ClSO_3)_2 + 6H_2O$ .

On evaporating the aqueous solution, after precipitating the barium with sulphuric acid, the free sulphonic acid crystallises out; this, when dried over sulphuric acid to remove water [of crystallisation, melted at 135°. Jünger and Klages (*Ber.*, 1896, 29, 315) have prepared the same acid from the chlorocymene obtained by the action of chlorine on cymene, by treating it with fuming sulphuric acid.

*Chlorocymene in Crude Carvenol*.—We have already called attention to the existence of a chlorine compound in crude carvenol; this occurs in relatively small quantity, but on purifying a large amount of carvenol, some 20 c.c. of a liquid insoluble in sulphuric acid was obtained. It is rich in chlorine, and as the purified carvenol is free from chlorine, we had thus separated the whole of the chlorinated substance from the carvenol. It was observed that this chlorine compound, when left in contact with strong sulphuric acid, gave colourless crystals, a circumstance which led us subsequently to investigate the action of sulphuric acid on chlorocymene, as described above. The liquid itself was found to distil at 95—101° under 10 mm. pressure, and at 210—216° under atmospheric pressure. When analysed, it gave, C=71·7; H=9·0, but, after being redistilled under 20 mm. pressure, two chief fractions were obtained boiling at 106—108° and 108—110° respectively.

On analysis of the fraction 106—108°, we found.

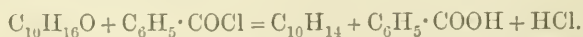
	Carbon.	Hydrogen.	Chlorine.
Found .....	72.2	9.4	18.4
Calculated for $C_{10}H_{13}Cl$ .....	71.2	7.7	21.0

Three grams of the substance were oxidised with nitric acid of sp. gr. 1.3, and the same chlorotoluic acid melting at  $200^{\circ}$  was obtained. The liquid also, like chlorocymene, is not acted on by permanganate of potash at the ordinary temperature except on long standing. There would thus seem to be little doubt that chlorocymene is contained in the liquid, but is mixed with some impurity. It is curious that the boiling point should be so constant, as cymene, which is the most likely impurity to be present, boils at a much lower temperature.

*Action of Benzoic Chloride on Carvenol.*—With the intention of preparing a compound ether of carvenol, on the supposition that carvenol is an alcohol, we treated that substance with benzoic chloride; 17.7 grams of carvenol and 20 grams of benzoic chloride were heated to boiling in a flask connected with an apparatus for absorbing the hydrogen chloride given off. After 2 hours heating, 4 grams of hydrogen chloride had been collected (theoretical amount 4.25 grams), and, on cooling, crystals separated, which were found to be benzoic acid; the filtered liquid was distilled under diminished pressure, and the distillation continued until the distillate began to come over solid. The principal portion of the distillate came over below  $100^{\circ}$  under 19.5 mm. pressure, and this, when distilled under atmospheric pressure, came over between  $176^{\circ}$  and  $186^{\circ}$ ; it contained chlorine, and smelled slightly of benzoic chloride. It was therefore washed with soda solution, dried with calcium chloride, and allowed to stand over metallic sodium. Distilled under a pressure of 32 mm., it boiled at  $86$ — $87^{\circ}$ , and under atmospheric pressure very constantly at  $179^{\circ}$ , and was free from chlorine.

	Carbon.	Hydrogen.
Found.....	89.6	10.8
Calculated for $C_{10}H_{14}$ .....	89.5	10.5

There is thus no doubt that the liquid is cymene. That it is paracymene was proved by the excellent test suggested by Widman, namely, the production of parahydroxyisopropylbenzoic acid by oxidation with potassium permanganate; only 1 c.c. of the cymene was taken for oxidation, and a good yield of the above-mentioned acid was obtained of melting point  $156^{\circ}$ . Thus it appears that the action of benzoic chloride on carvenol results in the formation to a considerable extent of paracymene, thus



We are further investigating the residue left on distilling off the cymene, which contains benzoic acid in quantity, to discover whether



any ethereal benzoate is formed. But, on the other hand, this action of benzoic chloride is consistent with our view that carvenol behaves as a tertiary alcohol.

*Carvenolsemicarbazone*.—The semicarbazone was prepared by acting on carvenol with semicarbazide hydrochloride and potassium acetate in dilute alcoholic solution; the compound began to come down after the lapse of 3 hours, and at the end of 24 hours a copious precipitate was obtained; this crystallised from alcohol in small, colourless plates melting at  $202-203^{\circ}$ .

	Found.	Calc. $C_{11}H_{19}N_3O$ .
Nitrogen.....	20.20	20.09

This action of semicarbazide points to the ketonic nature of carvenol. It thus appears to act, like phloroglucinol and other tautomeric substances of this nature, both as an alcohol and as a ketone.

*Reduction of Carvenol: Carvanol*.—Carvenol was reduced by metallic sodium in solution in absolute alcohol. Portions of 10 c.c. of carvenol dissolved in 50 c.c. of absolute alcohol were treated with 8 grams of sodium, the sodium being added in small portions at a time, and the contents of the flask cooled, as the action is very violent at starting; the last portions of sodium were added to the mixture heated to boiling to complete the action. On adding a few drops of water, the contents of the flask became solid, but when more water was added an oil separated; this was purified by distillation under diminished pressure. It distilled at  $100-110^{\circ}$ , and under atmospheric pressure at  $210-220^{\circ}$ , some  $15^{\circ}$  lower than carvenol. In order to ensure the reduction of all the carvenol, the product of the first reduction was again treated with sodium in alcoholic solution, the action of the sodium being much less violent than in the first treatment. On recovering the oil in the way just mentioned, it was found to distil at  $109-110^{\circ}$  under 14 mm. pressure. On analysis, it gave,

	Carbon.	Hydrogen.
Found .....	76.2	12.5
Calculated for $C_{10}H_{20}O$ .....	76.9	12.8

Carvanol, as we propose to call this substance, is a colourless liquid of sp. gr. 0.9128 at  $23.5^{\circ}$  (water at  $4^{\circ}$ ); it is very viscous, differing in this respect from carvenol, which is very mobile. It has a pleasant, aromatic odour and pungent, peppermint-like taste. It is a secondary alcohol, as is shown by its oxidation to a ketone, and forms an acetate having a fragrant smell resembling that of oil of vetiver.

*Oxidation of Carvanol: Carvanone*.—Twelve grams of carvanol were oxidised with potassium dichromate and sulphuric acid, according to the method described by Beckmann for the oxidation of menthol to

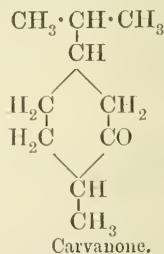
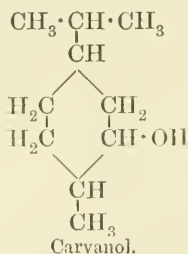


menthone; on completion of the oxidation, the mixture was distilled in steam; the oil, when collected and distilled under a pressure of 14 mm., came over at 94—100°, and at 214—219° under atmospheric pressure. On analysis, it gave,

	Carbon.	Hydrogen.
Found .....	77.3	11.5
Calculated for $C_{10}H_{18}O$ .....	77.9	11.7

Carvanone, the ketone of carvanol, was obtained as a slightly yellow liquid, very mobile, and resembling carvenol in odour; its sp. gr. at 25° was found to be 0.9065 (water at 4°). When treated with hydroxylamine hydrochloride and potash, it forms a crystalline oxime which melts at 104—105°. It also forms a semicarbazone when treated with semicarbazide hydrochloride and potassium acetate in dilute alcohol; this, after crystallisation from methylic alcohol, melted at 173°. Carvanone does not decolorise potassium permanganate in the cold, and appears to be a saturated compound.

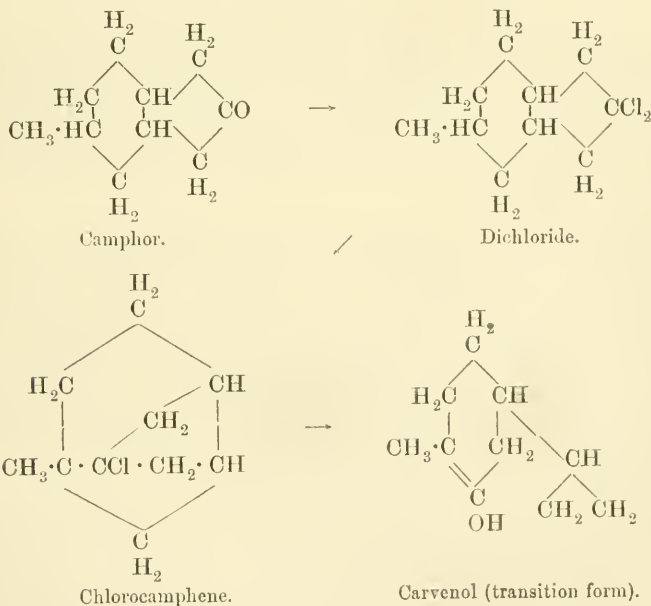
*Constitution of Carvanol and Carvanone.*—The conversion of carvenol into paracymene and chlorocymene [ $CH_3:Cl:C_3H_7=1:2:4$ ] by comparatively simple reactions, points to the conclusion that carvenol probably has the same carbon skeleton as cymene; this is further confirmed by the reduction of carvenol to carvanol when an addition of four hydrogen atoms takes place. Further, the saturated character of the ketone, carvanone, points to the conclusion that, inasmuch as its formula is  $C_{10}H_{18}O$ , it cannot be an open chain compound, but must be constituted of one closed ring and not more than one. Taking into account all these considerations, we are led to the conclusion that carvanol is a hexahydrocarvacrol, and carvanone the corresponding ketone. They would then be represented by the following formulæ.



differing from their respective isomerides menthol and menthone in the position of  $CH \cdot OH$  and  $CO$  groups which, in the case of menthol and menthone, are attached to the carbon atom adjacent to the isopropyl group.

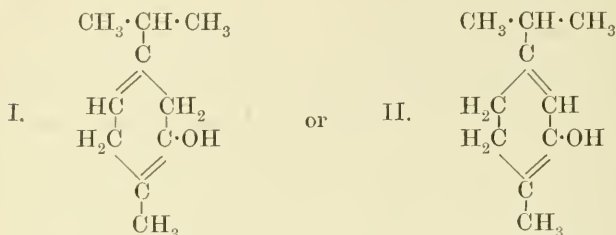
*Constitution of Carvenol and its Formation from Camphor.*—From the comparatively simple conversion of carvenol into paracymene and chlorocymene (carvacryl chloride), and since the reduced compound

carvenol is constituted of only one closed carbon chain, there seems no doubt that carvenol is actually a dihydrocarvaerol with two double linkings. The position of one double linking, owing to the tautomeric nature of carvenol, should be adjacent to the C(OH) grouping on one side or the other. This is, perhaps, as far as we can get from the properties of carvenol itself, but in considering its production from camphor we have a further means of arriving at its constitution, for camphor, being constituted of two closed rings, would have one of them broken to form carvenol, which has only one ring, if we suppose that carvenol is formed from camphor directly. But as we have shown, carvenol is formed from camphor through chlorocamphene. Chlorocamphene is a saturated compound of the formula  $C_{10}H_{15}Cl$  without double linkings, and must consequently be constituted of at least three closed rings. Therefore, to form carvenol from chlorocamphene, two closed rings must be broken. The mode in which this change may be brought about is explained by the following formulæ.



Here we should expect to find one of the double linkings in carvenol in the side chain. On the other hand, since carvenol ought to have an isopropyl group, and inasmuch as a  $CH_2$  group at the end of a chain has a tendency to pass into  $CH_3$ , by intramolecular change, there is no unwarranted assumption in supposing that the double-

linking migrates from the side chain into the ring, a change probably similar to that whereby carvol becomes converted into carvacrol. We should thus arrive at the two following alternative formulæ for carvenol.



Carvenol.

with the corresponding tautomeric forms in which the  $\begin{array}{c} \text{C}=\text{C} \\ | \quad | \\ \text{CH}_3 \quad \text{OH} \end{array}$  group becomes  $\begin{array}{c} \text{CH} \\ | \\ \text{CH}_3 \end{array} \text{—CO}$ .

We cannot, however, regard it as rigidly demonstrated that carvenol must have an isopropyl group and not an isopropylene or even trimethylene group. In the latter case, the change to an isopropyl group would occur subsequently when carvenol was converted into cymene or chlorocymene under the action of benzoic chloride or phosphorus pentachloride.

*Comparison of the Properties of Carvenol, &c., with Compounds already known.*—Numerous compounds of the formula  $\text{C}_{10}\text{H}_{16}\text{O}$  have been from time to time discovered, and to some of these carvenol bears a very close resemblance. In particular, two of these compounds, one obtained by Wallach from terpineol (*Annalen*, 1893, 277, 122), and the other, obtained by Semmler from tanacetone (*Ber.*, 1894, 27, 895), appear in their properties, and in those of the compounds derived from them, to be identical with carvenol and with each other. It seems to us a matter of considerable theoretical importance that terpineol, tanacetone, and camphor should be convertible into one and the same substance which is also isomeric with two of them. We give a table of comparison of these substances on the following page.

It will be seen from this table that carvenol closely resembles in properties both the carvenone obtained by Wallach from terpineol, and the carvotanacetone obtained by Semmler from tanacetone. We have not adopted either of these names, partly because the identity of the three substances may not be quite fully established, and partly because we wish by the termination *ol* to indicate the alcoholic

Compound $C_{10}H_{16}O$ .	Source.	Boiling point.	Specific gravity.	Semicarbazone.	Oxime.	
Carvenone (Wallach, <i>Ann.</i> , <b>277</b> , 122).....	Terpineol. } }	231—233°	0.926 at 19°	m. p. 200—201°	m. p. 91—92° {	reduced to tetrahydro-carveol.
Carvotanacetone (Semmler, <i>Ber.</i> , <b>27</b> , 895).....	Tanacetone. } }	228°	0.9373 at 17°	—	m. p. 92—93° {	reduced to tetrahydro-carvotanacetone.
Carvenol (Marsh & Gardner, <i>Trans.</i> , 1897, 290).....	Camphor. } }	230°	0.9372 at 19½°	m. p. 202—203°	—	reduced to carvanol.
Compound $C_{10}H_{16}O$ . Tetrahydrocarveol (Wallach, <i>loc cit.</i> ).....	Carvenone. } }	220°	0.90 at 23°	—	— {	thick oil oxidised to tetrahydrocarvone.
Tetrahydrocarvotanacetone (Semmler, <i>loc cit.</i> ).....	Carvotanacetone. } }	219—220°	0.9014 at 17°	—	—	thick oil.
Carvanol (Marsh and Hartridge) .....	Carvenol. } }	220°	0.9128 at 23½°	—	— {	thick oil oxidised to carvanone.
Compound $C_{10}H_{16}O$ . Tetrahydrocarvone (Wallach, <i>loc cit.</i> ).....	Tetrahydro-carvenol. } }	220—221°	0.9055 at 20°	m. p. 174°	m. p. 103° {	
Carvanone (Marsh and Hartridge) .....	Carvanol. } }	219°	0.9065 at 25°	m. p. 173°	m. p. 104—105° {	

character of the substance. We point out, in conclusion, that Wallach adopts for carvenone as the most probable formula (*Annalen*, 1893, 277, 129) the same formula, namely, No. 1, which we, from quite other considerations, have arrived at for carvenol.

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## LXXXVI.—*Optically Active Alkyloxypropionic Acids.*

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THE ethereal salts of active lactic acid, prepared by the action of alkyl iodides on silver lactate, exhibit a notably higher rotation than the lactates prepared by other methods (*Trans.*, 1895, 67, 916), and it has been recently shown (*Trans.*, 1898, 73, 296) that this is probably due to the active lactates, prepared by the silver salt method, being contaminated with small quantities of the corresponding alkyloxypropionates. This conclusion was based on experiments made with inactive silver lactate. Isopropylic iodide, which seems to be peculiarly prone to the abnormal interchange by which the alkyloxy-compounds are produced, yields, by its action on inactive silver lactate, such a considerable proportion of isopropylic isopropoxypropionate, that it is possible to isolate the acid from the product in the form of its metallic salts. Facts were also adduced (*loc. cit.*) to show that in the case of ethylic iodide and inactive silver lactate a similar reaction occurs, but to a smaller extent.

If this explanation of the high rotation of the active ethereal lactates, prepared in the manner referred to, is correct, it follows that the alkyloxypropionic acids must be substances of very high optical activity, as otherwise their presence as ethereal salts in admixture with the active lactates would be detected by analysis.

With the object of verifying this conclusion, and of contributing some data bearing on the problem of the quantitative relation of optical activity to chemical constitution, we thought it would be desirable to prepare and examine some of the active  $\alpha$ -alkyloxypropionic acids, these acids possessing a special interest with regard to this problem, on account of their relation to lactic acid and their simple constitution.

The most obvious method of obtaining the active alkyloxypropionic acids, by the action, namely, of sodium alkylate on the ethereal salts of the active  $\alpha$ -chloro- or bromo-propionic acids, being inapplicable on account of the racemisation which occurs during the process (*Trans.*,



1896, 69, 819), we had to adopt the tedious method of resolving the inactive alkyloxy-acids by means of alkaloids, a method which is unsatisfactory, as the activity of acids obtained in this way is sometimes far short of the maximum, even after prolonged fractional crystallisation of the alkaloid salts.

We carried out the resolution of inactive  $\alpha$ -ethoxypropionic acid with cinchonidine, and also with morphine, which lends itself still better to the process, an acid of somewhat higher activity being thus produced. In the cases of methoxy- and propoxy-propionic acids, morphine was the only alkaloid by which satisfactory resolutions could be effected.

*Preparation of Inactive  $\alpha$ -Ethoxypropionic Acid.*

The ethylic salt of this acid was prepared by Wurtz by the action of sodium ethoxide in alcoholic solution on ethylic  $\alpha$ -chloropropionate, and also by the action of ethylic iodide on ethylic potassiolactate (*Ann. Chim. Phys.*, 1860, [iii], 59, 169; 1861, 63, 103); similarly from ethylic  $\alpha$ -bromopropionate by Schreiner (*Annalen*, 1879, 197, 13). We followed Schreiner's method. The reaction does not proceed quantitatively, as Schreiner's remarks would lead one to expect; thus from 580 grams of bromopropionate, which was worked up in portions of 100 grams at a time, we obtained in all only 240 grams of ethylic ethoxypropionate (b. p. 155—157°), a little over 50 per cent. of the calculated yield. The boiling point of the pure substance is 155° at 760 mm. The small yield was probably due to the formation of ethylic acrylate; on distillation, a considerable fraction of liquid was, in fact, always collected between the boiling point of alcohol and that of the ethoxypropionate.

The ethereal oil was hydrolysed by heating it with 10 per cent. aqueous potassium hydroxide solution; the hydrolysis may be accelerated by adding some alcohol, but the product in this case becomes coloured. On completion of the hydrolysis, the liquid was neutralised with dilute sulphuric acid, concentrated to a syrup, acidified, and shaken with ether, which readily extracts the acid. Some of it was converted into the crystalline calcium salt for analysis; the dry salt was found to contain 14.72 per cent. of calcium, the calculated number being 14.60. As the acid undergoes some decomposition on being distilled, no attempt was made to free it from water, the wet syrup being used for our experiments.

Comparative experiments made by neutralising equal quantities of an aqueous solution of the acid with various alkaloids, showed that the alkaloid salts in general were very soluble. The salt of cinchonine proved to be a gum; the salts of brucine and strychnine crystallised,

but only from very concentrated solutions; cinchonidine and morphine gave deposits, respectively, of long, matted needles, and of well-shaped prisms, from fairly concentrated solutions, whilst quinine and quinidine could not be dissolved to a neutral solution. When the acid was half neutralised with alkaloid, quinine and quinidine gave crystalline deposits from dilute solution, but the salts of the other alkaloids crystallised with difficulty under this condition. Of the salts procurable in neutral solution, those of cinchonidine and morphine seemed to be the most crystallisable, and these alkaloids were therefore chosen for experiments on the resolution of the acid into its active components.

*Resolution of Ethoxypropionic Acid with Cinchonidine.*

Our first experiments showed that the cinchonidine salt of the dextro-acid was the less soluble, but that prolonged crystallisation of the alkaloid salts would be requisite to secure the production of pure active acid. We, therefore, conducted an experiment on a larger scale.

A warm, aqueous solution containing about 128 grams of acid was neutralised with 316 grams of cinchonidine; on evaporating and cooling, 159 grams of crystalline salt separated, that is to say, more than a third of the total quantity present. The salt thus obtained was repeatedly recrystallised, the increase of activity after each recrystallisation being observed by decomposing 2 grams of the dried salt with ammonia, evaporating the solution until nearly neutral, and then diluting it until it exactly filled the 200 mm. tube in which the observations were taken. After three recrystallisations, the quantity of cinchonidine salt was reduced to 55 grams, and the observed rotation of the ammonium salt had increased from  $+3.00^\circ$  to  $+3.85^\circ$ . The quantity of material did not admit of the process being carried further, but judging from the fact that on again recrystallising a portion of it, only a small increase of activity occurred, it appeared probable that the maximum activity had been nearly reached. A further crop of 25 grams of similar activity was obtained from the mother liquors remaining from the recrystallisations; a second crop of crystals, on the other hand, obtained from the original mother liquor, gave a rotation, as ammonium salt, of only  $+2.15^\circ$ .

*Calcium d-Ethoxypropionate.*—The purest cinchonidine salt, weighing 70 grams, was converted into calcium salt by removal of the cinchonidine with ammonia, treatment of the ammoniacal solution with calcium hydroxide, and removal of the excess of the latter with carbonic anhydride. The salt, which seemed to be more soluble than the inactive form, separated from a concentrated solution, on cooling,

in the form of microscopic, flat prisms or needles. An analysis showed that, like the inactive salt, it contained  $2\text{H}_2\text{O}$ .

Found,  $\text{H}_2\text{O} = 11.42$ , Ca (in salt dried at  $120-140^\circ$ ) =  $14.54$  per cent. Calculated for  $\text{C}_{10}\text{H}_{18}\text{O}_6\text{Ca} + 2\text{H}_2\text{O}$ ,  $\text{H}_2\text{O} = 11.61$ ; Ca =  $14.60$  per cent.

A recrystallised specimen gave the numbers  $11.60$  and  $14.75$ . Determinations of specific rotation gave the following results for the anhydrous salt,  $c = 10.375$ ,  $[\alpha]_D = +42.55^\circ$ ;  $c = 4.15$ ,  $[\alpha]_D = +45.66^\circ$ . It was found impossible to raise the activity of the calcium salt by crystallisation; three successive crops from the same solution, and one of these after recrystallisation, all showed, for corresponding concentration, practically the same specific rotations as those quoted.

*d-Ethoxypropionic Acid*.—The acid was obtained from the calcium salt by precipitating with potassium carbonate, evaporating the solution of the potassium salt to a syrup, acidifying with dilute sulphuric acid, and extracting with ether. Determinations of the specific rotation of aqueous solutions gave the results which follow, the concentrations being found by means of standard alkali, and the temperature of observation being  $15^\circ$ ;  $c = 25.812$ ,  $[\alpha]_D = +53.83$ ;  $c = 10.325$ ,  $[\alpha]_D = +52.01^\circ$ ;  $c = 5.162$ ,  $[\alpha]_D = +52.11^\circ$ .

*Sodium d-Ethoxypropionate*.—The acid was converted into sodium salt by exact neutralisation with sodium hydroxide solution, and the concentrations of the aqueous solutions used for the following determinations of specific rotation at  $15^\circ$  were found by evaporating aliquot portions and drying the residue at  $110^\circ$ ;  $c = 12.141$ ,  $[\alpha]_D = +45.88^\circ$ ;  $c = 4.857$ ,  $[\alpha]_D = +45.91^\circ$ . Estimations of sodium in the dried residues by conversion into sulphate gave  $16.58$  and  $16.48$ , the calculated percentage being  $16.43$ .

*Silver d-Ethoxypropionate*.—The silver salt was made by neutralising the aqueous solution of the acid with silver carbonate; like the inactive salt, it is readily soluble in hot water, much less so in cold, and it crystallises well in the form of a felted mass of needles. The salt dried over sulphuric acid was found to contain  $47.98$  per cent. of silver, and a combustion gave the following results.

Found.....C =  $26.41$ ; H =  $4.20$ ; Ag =  $47.90$  per cent.

Calculated C =  $26.67$ ; H =  $4.00$ ; Ag =  $48.00$  „

A solution saturated in the cold showed the following specific rotation:  $l = 4$ ,  $c = 1.98$ ,  $\alpha = +2.25^\circ$ , hence  $[\alpha]_D = +28.41^\circ$ .

*l-Ethoxypropionic Acid*.—An attempt was made, but without success, to isolate *l*-ethoxypropionic acid from the original mother liquor of the cinchonidine salt which had given the dextro-acid. This liquor still contained a large proportion of the latter acid which it was impossible to eliminate by crystallisation; the cinchonidine was therefore re-

moved by ammonia, and the whole converted into calcium salt, which was subjected to prolonged and systematic fractional crystallisation in the hope that the inactive salt might be mostly removed by its smaller solubility. A large proportion of feebly active salt was in fact thus eliminated, but the most levorotatory crop obtained had a specific rotation of only  $-32.8^\circ$ , the rotation found for the dextro-salt under similar conditions being  $+42.55^\circ$ . The attempt to obtain the pure lævo-acid by this method was therefore abandoned.

*Resolution of Ethoxypropionic Acid with Morphine.*

Experiments, made by neutralising the most active acids obtained as above, showed that the morphine salt of the lævo-acid was gummy, and had but little tendency to crystallise, whilst that of the dextro-acid crystallised readily in short prisms. These experiments also proved that the dextro-acid prepared by means of cinchonidine was probably not far from pure, the treatment with morphine having raised the specific rotation of its calcium salt only from  $+45.66^\circ$  to  $+47.52^\circ$  ( $c = 4.03$ ).

In preliminary experiments on the resolution of the inactive acid, we found that the dextro-form could be obtained by crystallisation either from aqueous or slightly acid alcoholic solution, but as the latter method gave a better result, it was employed for the resolution on a larger scale.

A quantity of inactive acid, which required 165 grams of morphine for neutralisation, was dissolved in 200 grams of dry methylated spirit; the alkaloid was dissolved in the boiling liquid, and then a slight excess of acid added. Concentration of the solution is undesirable, owing to the darkening of the liquid on prolonged heating. On cooling the solution, the salt crystallised at once; two successive crops were removed and dried. To test the activity of these and subsequent crystallisations, the same method was always employed; 1.5 grams of the salt was decomposed with ammonia, and the solution was freed as far as possible from small quantities of dissolved morphine by evaporation; the nearly neutral filtered solution was then diluted so as just to fill the 200 mm. tube. The observations were as follows: 1st crop 130 grams,  $+1.83^\circ$ ; 2nd crop, 13 grams,  $+1.15^\circ$ ; 1st recrystallisation of these two crops mixed, 72 grams,  $+3.37^\circ$ ; 2nd, 53 grams,  $+3.57^\circ$ ; 3rd, 35 grams,  $+3.42^\circ$ , and another crop from the same solution, 8.5 grams,  $+3.52^\circ$ . The recrystallisations must be conducted in aqueous solution, as the alcoholic solutions of the neutral morphine salt dissociate on heating, much morphine being precipitated. The maximum activity obtainable by crystallisation had evidently been reached, but the yield of active material was small. The recrystallised



morphine salt, in all 39 grams, was decomposed with ammonia, and after removal of the morphine, the solution, which was kept just faintly alkaline, was concentrated, filtered from traces of alkaloid, acidified with sulphuric acid, and shaken with ether.

The *d*-ethoxypropionic acid obtained from the ethereal solution was converted into calcium salt by neutralisation with calcium carbonate, and an analysis of the salt dried at  $110^{\circ}$  gave 14.66 per cent. of calcium instead of the calculated number 14.60. This salt was used for the specific rotations which are quoted below, and from it were prepared the acid, and the sodium and barium salts of which the specific rotations are also given. The acid was obtained from the calcium salt as a syrup in the manner previously described, but the attempt to free it from water was not made, as this could only have been done by distillation, which would probably have caused decomposition or racemisation. The combustion of the silver salt made from it, quoted below, affords evidence of its purity. The sodium and barium salts were made from the acid in the usual manner. The former remains in the form of a gum when its solutions are evaporated, which, however, becomes an amorphous solid on being dried at  $100-110^{\circ}$ ; an estimation of sodium gave 16.53 per cent. instead of the calculated number 16.43. The solution of the barium salt also leaves a gum when evaporated, which on heating dries up to an amorphous solid. An estimation of barium gave the number 36.96, the calculated percentage being 36.93. Finally, the acid was recovered from the solutions of the salts by acidification and extraction with ether. The crystalline *silver salt* prepared from it gave the following results on combustion.

Found .....C = 26.60 ; H = 4.15 ; Ag = 47.95 per cent.

Calculated C = 26.67 ; H = 4.00 ; Ag = 48.00     ,,

The original mother liquor of the morphine salt, from which the dextrorotatory acid was obtained, gave a levorotatory acid mixed with much inactive acid, which it seemed impossible to remove.

The concentrations of the solutions, used in the polarimetric observations given below, were found in the case of the acid by means of a decinormal solution of sodium hydroxide, and in the case of the salts by evaporating known volumes of them to dryness, and estimating the metal in the residue. The numbers refer, of course, to the anhydrous compounds; the letter N signifies *normal*. The more dilute solutions were prepared by suitable dilution of the most concentrated. The observations on the silver salt are given for comparison, although it was made from the somewhat less active acid obtained with the aid of cinchonidine.



*d*-Ethoxypropionic Acid.

	<i>c</i>	<i>l</i>	$\alpha$	$[\alpha]_D$	$[\alpha]_D \frac{M}{100}$
<i>Acid.</i>	29.374	1	+16.73°	+56.96°	+67.21°
( <i>M</i> =118)	11.750 = N. nearly.	2	12.76	54.30	64.07
( <i>t</i> =11—12°)	5.875 = $\frac{1}{2}$ N. „	1	3.18	54.13	63.87
	2.350 = $\frac{1}{5}$ N. „	2	2.50	53.19	62.76
<i>Sodium salt.</i>	17.965	1	+8.64°	+48.09°	+67.33°
( <i>M</i> =140)	7.186 = $\frac{1}{2}$ N. nearly.	2	7.00	48.71	68.19
( <i>t</i> =10—11°)	3.593 = $\frac{1}{4}$ N. „	2	3.53	49.12	68.77
<i>Barium salt.</i>	19.3625	2	+13.27°	+34.27°	+63.57°
( <i>M</i> = $\frac{271}{2}$ )	7.7450	2	5.64	36.41	67.54
( <i>t</i> =14—15°)	3.8725	2	2.85	36.80	68.26
<i>Calcium salt.</i>	26.875 = 2 N. nearly.	1	+10.32°	+38.40°	+52.61
( <i>M</i> = $\frac{271}{2}$ )	10.750 = $\frac{4}{5}$ N. „	1	5.01	46.60	63.84
( <i>t</i> =10—11°)	5.375 = $\frac{2}{5}$ N. „	2	5.20	48.37	66.27
<i>Silver salt.</i>	1.980	4	+2.25°	+28.41°	+63.92°
( <i>M</i> =225)					
<i>Sodium salt in alcohol.</i>	18.138	2	+5.36°	+14.78°	+20.69°
( <i>M</i> =140)	6.046	2	2.98	24.64	34.50
( <i>t</i> =11—12°)	3.6275	2	2.19	30.19	42.27

*Preparation of Inactive  $\alpha$ -Methoxypropionic Acid.*

Schreiner succeeded in preparing pure, inactive ethylic methoxypropionate from ethylic bromopropionate. We thought it, however, safer to use methylic  $\alpha$ -bromopropionate as the starting point, in order to avoid any risk (compare *Trans.*, 1888, 53, 391) of the formation of the ethoxy-compound.

The details of the preparation were the same as in the case of the ethoxy-compound, except that the mixture of bromo-ethereal salt with the methoxide was heated to complete the reaction, and that, the liquid being then neutral, the passage of carbonic anhydride through it was omitted.

The yield of methoxypropionate was small, only 186 grams of it, boiling at 130—135°, being obtained from 500 grams of bromopropionate, that is to say, about 53 per cent. of the calculated yield. The boiling point, according to Markownikoff and Krestownikoff, is 135—138° (*Annalen*, 1881, 208, 343). The presence of water could

not be the cause of the small yield, as the methylic alcohol was dried with barium oxide before use. The acid was obtained from the ethereal salt in the same way as the ethoxy-compound. A portion of it, having been neutralised with calcium carbonate, left on evaporation a residue which, when dried at  $110^{\circ}$ , contained 16.21 per cent. of calcium. The calculated number for calcium methoxypropionate is 16.26.

Preliminary experiments on the inactive acid showed that the strychnine salt crystallised only from solutions of gummy consistency, and that the quinine salt, although it crystallised readily, did not effect resolution; the neutral quinidine salt was deposited in long, fibrous needles from aqueous solutions of syrupy consistency; 7 grams of these crystals gave an ammonium salt solution, which, when evaporated so as to fill a 200 mm. tube, showed the rotation  $-0.61^{\circ}$ , and the mother liquor, similarly treated, gave the rotation  $+0.98^{\circ}$ . The cinchonidine salt crystallised from moderately concentrated aqueous solution in bundles of long needles, which were recrystallised four times, and thus reduced to about one-eighth of the original quantity; 2 grams of this, converted into ammonium salt and examined as above, gave the rotation  $-2.27^{\circ}$ . Ammonium and calcium salts from the original mother liquor were dextrorotatory. The resolution in the case of both these alkaloids was very imperfect.

#### *Resolution of $\alpha$ -Methoxypropionic Acid with Morphine.*

An aqueous solution of the acid neutralised with morphine gives, on evaporation and long standing, only a gummy salt. In nearly neutral alcoholic solution, a crystalline deposit is readily obtained in the form of short prisms, consisting mainly of the salt of the *lævo*-acid. A half-neutralised solution gives the same result, but the quantity of salt obtained is less. Under certain conditions, however, the deposit from the neutral solution contains only inactive acid, which is probably due to the formation of a *partially racemic* salt (*Ber.*, 1898, 31, 937, 1969). Thus in one of our experiments, after removing two crops of crystals, which consisted mainly of the salt of the *lævo*-acid, the mother liquor, which now contained the *dextro*-acid in large excess, gave a third crop containing only inactive acid, and this crop, on recrystallisation, although the solution was sown with a nucleus of the salt of the *lævo*-acid, again yielded nothing but inactive acid. The same phenomenon was observed in the following experiment on a larger scale.

A hot alcoholic solution of the acid was neutralised by adding 158 grams of morphine. On cooling, a large crop of crystals was deposited, weighing 150 grams when dry; the acid from this was found to be inactive. By recrystallisation, the quantity of salt was reduced to 114 grams, but the acid from this was only slightly laevorotatory. The whole of the salt was then returned to the original mother liquor, and after filtering off some morphine which did not dissolve, it was crystallised from more dilute alcoholic solution; resolution had now occurred. 1.5 grams, examined as ammonium salt in a 200 mm. tube, gave the rotation  $-2.25^\circ$ , and a second small crop contained acid of nearly the same activity. This salt was then recrystallised three times from alcohol, the test experiments giving, in order, the rotations  $-3.20^\circ$ ,  $-3.45^\circ$ ,  $-3.40^\circ$ . The resolution had reached its limit, and we accordingly used this material for obtaining the laevo-acid, the observations on which are given below.

The original mother liquor of the salt of the laevo-acid gave a crystalline morphine salt which yielded a dextrorotatory acid, but the activity of the acid increased so slowly on recrystallising the salt, that the preparation of the pure dextro-acid by this method had to be abandoned.

The morphine salt of the laevo-acid, which gave the rotation  $-3.40^\circ$ , was converted into the acid, and into calcium and sodium salts in the same way as in the case of ethoxypropionic acid. The acid was a syrup; the *calcium salt* was apparently more soluble than the corresponding ethoxypropionate, its solution on concentration giving a jelly-like, transparent mass which solidified on further evaporation. An estimation of calcium as sulphate gave 15.99 per cent. of calcium instead of the calculated number, 16.26. The *sodium salt* resembled the ethoxy-compound; the percentage of sodium found in it, estimated as sulphate, was 18.38, the calculated number being 18.25. Some of the acid which was finally recovered from the salts was converted into *silver salt* by neutralisation with silver carbonate; it crystallised in needles on cooling the hot solution. The percentage of silver in it was found to be 51.01, and it gave the following results on combustion.

Found.....C = 22.86; H = 3.36; Ag = 50.95 per cent.

Calculated C = 22.75; H = 3.32; Ag = 51.18     ,,

The solutions used for the following polarimetric observations were prepared, and their concentrations were determined in the manner indicated under ethoxypropionic acid.

## 1-Methoxypropionic Acid.

	<i>c.</i>	<i>l</i>	$\alpha$	$[\alpha]_D$	$[\alpha]_D \frac{M}{100}$
<i>Acid.*</i> ( <i>M</i> =104) ( <i>t</i> =12—13°)	13.475	1	-9.58°	-71.09°	-73.93°
	5.390 = $\frac{1}{2}$ N. nearly.	2	7.59	70.41	73.23
	2.695 = $\frac{1}{4}$ N. „	2	3.79	70.31	73.12
<i>Sodium salt.</i> ( <i>M</i> =126) ( <i>t</i> =11°)	16.530	1	-8.17°	-49.43	-62.28°
	6.613 = $\frac{1}{2}$ N. nearly.	2	6.72	50.81	64.02
	3.306 = $\frac{1}{4}$ N. „	2	3.44	52.03	65.56
<i>Calcium salt.</i> ( <i>M</i> = $2\frac{1}{2}$ N.) ( <i>t</i> =10°)	9.530 = $\frac{4}{5}$ N. nearly.	1	-3.63	-38.09°	-46.85°
	4.765 = $\frac{2}{5}$ N. „	2	4.14	43.44	53.43

\* See reference to these observations on the free acid, p. 876.

## Preparation of Inactive Propoxypropionic Acid.

The propylic salt of this hitherto unknown acid was prepared by the action of a solution of sodium propoxide on propylic  $\alpha$ -bromopropionate. The method which gave the best results was as follows. Two hundred grams of the bromopropionate were added gradually to a hot solution of 26 grams of sodium in 400 grams of propylic alcohol. When the calculated quantity of sodium was used, some bromopropionate remained unaltered. The mixture having been heated for an hour, a current of carbonic anhydride was passed through it; water was then added, and the oil, which separated readily, was distilled fractionally after being dried with potassium carbonate. The fractions boiling at 186—190°, which contained the propylic propoxypropionate and were used for our experiments, amounted to only 55 per cent. of the calculated yield. The liquid boiled mostly at 187—188°, and an analysis of this portion gave the following results.

Found: I. C=61.78; H=10.96 per cent.

II. C=61.86; H=10.74 „

Calculated, C=62.07; H=10.34 per cent.

A gummy substance which separated from the ethereal salt in the course of distillation was found to be an alkaline salt of propoxypropionic acid. A calcium salt, made from it, contained 13.22 per cent. of calcium; the calculated percentage is 13.25. The acid, which was

obtained from the ethereal salt as in the previous cases, is less soluble in water than the other two acids, and separates at once as an oil on adding dilute sulphuric acid to a concentrated solution of the potassium salt. The *calcium salt*, which is also much less soluble in water than the corresponding methoxy- and ethoxy-salts, crystallises in scaly plates containing  $2\text{H}_2\text{O}$ , which is lost at  $105^\circ$ . Analysis gave the following results.

Found: I.  $\text{H}_2\text{O} = 10.37$ ;  $\text{Ca}$  (in dry salt)  $= 13.21$  per cent.

II.  $\text{H}_2\text{O} = 10.41$ ;  $\text{Ca} = 13.24$  per cent.

Calculated for  $\text{C}_{12}\text{H}_{22}\text{O}_6\text{Ca} + 2\text{H}_2\text{O}$ ;  $\text{H}_2\text{O} = 10.65$ ;  $\text{Ca} = 13.25$  per cent.

The *silver salt*, made by neutralising the acid with silver carbonate, crystallises in fine needles sparingly soluble in cold water. An estimation of silver gave  $\text{Ag} = 45.26$  per cent. The results obtained by combustion were as follows.

Found.....  $\text{C} = 30.14$ ;  $\text{H} = 5.05$ ;  $\text{Ag} = 45.45$  per cent.

Calculated  $\text{C} = 30.13$ ;  $\text{H} = 4.60$ ;  $\text{Ag} = 45.19$  „

The *barium salt* is a gum; the *strontium* and *magnesium salts* are crystalline, the former crystallising in long, flat prisms, the latter in feathery aggregates. Solutions of the copper and cadmium salts leave gums on evaporation.

The salts of cinchonine and quinidine were found to be gums; that of strychnine crystallised, but only from a very concentrated solution. The cinchonidine salt crystallised from a concentrated aqueous solution, and resembled the corresponding salts of the other two acids, but resolution was effected to only a very slight extent. A neutral solution containing 110 grams of the alkaloid gave a crop of 53 grams; on testing 2 grams of this by conversion into ammonium salt, as before, the rotation was only  $-0.33^\circ$ , and it rose very little on recrystallisation. The salt from the original mother liquor, similarly tested, gave a small dextrorotation.

#### *Resolution of Propoxypropionic Acid with Morphine.*

As in the case of methoxypropionic acid, this salt could not be made to crystallise from water. A first attempt to crystallise it from alcohol was also unsuccessful; on allowing the alcohol to evaporate over sulphuric acid, nothing but morphine crystallised out. On filtering off the alkaloid, however, and adding benzene, a hard crust of prismatic crystals was deposited, which proved to be the salt of the dextro-acid. After repeated trials, we found that, by adding the alkaloid to a more concentrated hot alcoholic solution of the acid, the latter being care-



fully kept in slight excess, the precipitation of morphine was avoided, and resolution was effected without the use of benzene, the salt of the dextro-acid being also first deposited in this case. Using 100 grams of alcohol (methylated spirit) for every 85 grams of morphine, nearly a half of the total neutral salt present crystallised quickly, on cooling, in the form of six-sided plates; the salt was recrystallised from water. The following numbers, giving the weights of salt deposited on successive recrystallisations, and the corresponding rotations shown by the ammonium salt solutions from 1.5 grams morphine salt in the 200 mm. tube, will show the progress of the resolution.

1st crop .....	139	grams;	rotation, + 2.08°
1st recrystallisation .....	107	„ „	+ 3.03
2nd „ .....	85	„ „	+ 3.35
3rd „ .....	62	„ „	+ 3.50
4th „ .....	38	„ „	+ 3.75

The quantity of material would not admit of the recrystallisation being carried further, and the salt showing the rotation + 3.7° was accordingly used for preparing the dextro-acid on which our observations were made. We think the acid was not far from its maximum activity.

The acid obtained from the original mother liquor of the morphine salt was levorotatory, but it was mixed with so much inactive acid that it was impossible to purify it.

The *d*-propoxypropionic acid was obtained from the morphine salt, and its calcium and sodium salts were prepared in the same way as in the case of the other two acids. The acid is a syrup, less soluble in water than its ethoxy-homologue. The *calcium salt*, in appearance, resembles the corresponding ethoxypropionate, but it is less soluble in water. An estimation of calcium in the salt, dried at 110°, gave  $\text{Ca} = 13.31$ , the calculated number being 13.25. The *sodium salt* is like the same salt of the other two acids. When dried at 115°, it contained 15.01 per cent. of sodium, the calculated percentage being 14.94.

The acid was finally recovered from the salts, and part of it converted into the *silver salt*; this is deposited in masses of felted needles on cooling a hot aqueous solution. A combustion was made with the following result.

Found.....  $\text{C} = 29.98$  ;  $\text{H} = 4.67$  ;  $\text{Ag} = 45.30$  per cent.

Calculated  $\text{C} = 30.13$  ;  $\text{H} = 4.60$  ;  $\text{Ag} = 45.19$  „

The solutions employed for the following observations were prepared as previously indicated.

*d*-Propoxypropionic Acid.

	<i>c</i>	<i>l</i>	<i>a</i>	$[\alpha]_D$	$[\alpha]_D \frac{M}{100}$
<i>Acid.</i> ( <i>M</i> = 132) ( <i>t</i> = 10°)	11.450	1	+6.37°	+55.63°	+73.43°
	4.580	2	5.00	54.58	72.05
	2.290	2	2.50	54.58	72.05
<i>Sodium salt.</i> ( <i>M</i> = 154) ( <i>t</i> = 11–12°)	30.750 = 2 N. nearly.	1	+15.05°	+48.94°	+75.36°
	12.300 = $\frac{4}{5}$ N. ,,	2	12.46	50.65	78.00
	4.920 = $\frac{8}{25}$ N. ,,	2	5.06	51.42	79.19
	2.460 = $\frac{4}{25}$ N. ,,	2	2.53	51.83	79.82
<i>Calcium salt.</i> ( <i>M</i> = $\frac{210.5}{2}$ ) ( <i>t</i> = 9°)	12.010 = $\frac{4}{5}$ N. ,,	1	+5.83	+48.54°	+73.29°
	6.005 = $\frac{2}{5}$ N. ,,	2	6.09	50.71	76.57

*Discussion of Results.*

Chr. Winther has propounded an ingenious theory of the resolution of racemic compounds (*Ber.*, 1895, 28, 3000), in which he endeavours to show precisely how the relative configurations of an alkaloid and the two oppositely active forms of an acid determine the different solubilities of the two salts produced by their combination. It follows as a deduction from the theory, that the alkaloids are divisible into two classes, according as they form the less soluble salt with one or other of the oppositely active forms of an acid, and that active acids (dextro- or laevo-, as the case may be) possessing similar configuration will behave similarly, with respect to the solubility of their salts, towards the members of each class of alkaloids. Thus quinine, quinicine, quinidine, strychnine, and brucine, when used for the resolution of the racemic forms, will precipitate *d*-tartaric acid and acids of corresponding configuration; cinchonine, cinchonidine, cichonicine, and morphine, on the other hand, will precipitate the oppositely configured forms.

The results of our experiments on the resolution of the alkyloxypropionic acids are well adapted to test the validity of these conclusions, for the acids are alike in constitution; their relative configuration is known, the similarly active acids having similar configuration;\* and

\* The production of small quantities of ethereal alkyloxypropionates in the preparation of ethereal lactates from silver lactate raises the activity of the product, hence the ethereal alkyloxypropionates and lactates of similar rotation have the same configuration, assuming, as is probable, that no change of configuration occurs in the course of the reaction referred to.

finally, as monobasic acids, their alkaloid salts are exempt from the abnormal solubilities which, according to Winther's theory, may be exhibited by the normal salts of unsymmetrical dibasic acids.

Our results may be tabulated as follows,

			Cinchonidine.	Morphine.	Quinidine.
Methoxy-acid	...	...	—	—	—
Ethoxy-acid	...	...	+	+	
Propoxy-acid	...	...	—	+	

the signs + and — indicating which of the two forms of each acid, dextro- or levo-, yields the less soluble salt of the alkaloid heading the column. It is evident that the results do not at all accord with the conclusions from the theory, for in that case all the signs in the first two columns should be the same, and that under quinidine different from the others.

Winther proposes to use his theory as a means of discovering the configuration of active compounds. The method, considering the uncertain basis of the theory, is certainly hazardous, as E. Fischer has already pointed out (*Ber.*, 1896, 29, 1379), and we may take this opportunity of indicating some erroneous results to which it leads. Winther (*loc. cit.*, p. 3912) concludes, from the behaviour of the alkyloxysuccinic acids with alkaloids, that the levo-forms of these acids have the same configuration as *d*-tartaric acid.\* It is true that, in the first instance, certain considerations led us to express the view that the *d*-alkyloxysuccinic acids probably corresponded to ordinary malic acid, and therefore, taking into account the known relation between the malic and tartaric acids (Bremer, *Ber.*, 1875, 8, 1594), to *l*-tartaric acid, which accords with Winther's conclusion. We have since pointed out, however, (*Trans.*, 1898, 73, 301) that our opinion was incorrect, for ordinary malic acid gives the *l*-alkyloxysuccinic acids, which therefore correspond to *l*-tartaric acid.

With regard to the degree of accuracy to be attached to the numerical data we have quoted, it must be kept in mind that the resolutions of the acids were probably not quite complete, more particularly in the case of the propoxy-acid, and that the numbers may, therefore, be somewhat too low. We believe, however, that the error is not great.

Referring to our polarimetric observations, the most striking point is the very great increase of optical activity which attends the replacement of the alcoholic hydrogen of lactic acid by an alkyl group. As there is no change of sign of rotation in passing from the lactates to the

\* The sign *d*- has been prefixed to the alkyloxy-acids on p. 3013 in Winther's paper, evidently in mistake for *l*-; similarly in the table, p. 3010, under the heading strychnine, *l*- should be prefixed to methoxysuccinic acid instead of *d*-.

alkyloxypropionates, the effect of the introduction of the alkyl group may be seen by comparing the molecular rotations of the alkali salts in dilute solution. The molecular rotation of the lactic acid ion is about  $14.5^\circ$ ; that of sodium ethoxypropionate in about  $N/4$  solution is  $68.77^\circ$ . A comparison of the ethereal lactates and alkyloxypropionates, observations on which we hope to publish shortly, shows a still greater increase of activity, as does also a comparison of the free acids, in which a change of sign attends the substitution. The replacement of hydrogen by an alkyl group produces, in fact, a greater rise of rotation than its replacement by an acid radicle, such as acetyl, or the substitution of chlorine or bromine for hydroxyl. Similarly, the conversion of malic into alkyloxysuccinic acids produces a striking rise of optical activity.

Increase in the weight of the introduced alkyl group produces, as might be expected, a very much smaller, although distinct, rise of molecular rotation, the numbers found in the most dilute solutions of the sodium salts being in the order of increasing molecular weight  $65.56^\circ$ ,  $68.77^\circ$ ,  $79.82^\circ$ . The molecular rotations of the calcium salts in solutions of equivalent concentration stand in the same order, as do also those of the free ethoxy- and propoxy-acids. The molecular rotation of the free methoxy-acid, on the other hand, is slightly higher even than that of the propoxy-acid at equivalent concentration. We cannot, however, at present attach any significance to the observations made on the free methoxy-acid. Being struck with its exceptional behaviour, we recovered the acid from its salts, and redetermined its rotation, and also that of the calcium salt made from the recovered acid. We then found that the specific rotation of the acid had risen greatly, namely, from  $-70.31^\circ$  to  $-104.46^\circ$ , but the rotation of the calcium salt did not differ materially from that previously found. The ethoxy-acid, which was also recovered from its salts, showed no anomaly of this kind. We are preparing larger quantities of the methoxy-acid for further investigation.

It will be seen that the rotations of the salts rise with dilution, and in general confirm the validity of the law of Oudemans and Landolt. The molecular rotations, for example, of the sodium, barium, calcium, and silver ethoxypropionates, in the most dilute solutions examined, are respectively  $68.77^\circ$ ,  $68.26^\circ$ ,  $66.27^\circ$ ,  $63.92^\circ$ . The silver salt, as already stated, was made with a somewhat less active acid than the other salts. The rotations of the free acids, on the other hand, decrease slightly with dilution. The opposite behaviour of the salts and acids on dilution of their aqueous solutions corresponds with the effect of alcohol on their respective rotations, this solvent causing, as might be expected from its influence on molecular association and electrolytic dissociation, a fall in the rotation of the salts and a rise in that of

the acids. Thus the specific rotation of sodium ethoxypropionate, which in water is  $49.12^\circ$ , becomes in alcoholic solution at about the same concentration,  $30.19^\circ$ , whilst that of the acid is raised from  $54.13^\circ$  in water to  $62.41^\circ$  in a solution containing equal parts of alcohol and water.

With regard to the comparative effect of varying concentration on aqueous solutions of lactic acid and the alkyloxypropionic acids, the latter, which are not subject to anhydride formation or other changes attributable to the hydroxyl group, should exhibit a more constant rotation. It will be seen from our observations on the free acids that, considering the high numbers representing their activity, the changes on dilution are comparatively slight. In investigating the rotations of the metallic lactates (*Trans.*, 1895, 67, 616), the abnormal behaviour of some of the salts led us to the conclusion that their increase of rotation on dilution was not to be accounted for by electrolytic dissociation alone, but was due also to some other factor, probably the breaking up of complex molecules, the formation of which, in concentrated solution, might be favoured by the hydroxyl group. The rotation of calcium lactate, for example, is not only much less than that of strontium and barium lactates, but on dilution shows no signs of approaching the common maximum nearly reached by these and the alkali salts. This anomaly, it will be seen, disappears in the calcium alkyloxypropionates. The behaviour of calcium ethoxypropionate is quite similar to that of the barium and sodium salts, taking into account its probably smaller degree of dissociation, and the same may be said of the propoxy-salt.

With regard to the methoxy-acid, the molecular rotation of its calcium salt on further dilution would also, no doubt, approach that of its sodium salt, but it will be seen that the difference between the rotations of the two salts is much greater than the difference between the rotations of the corresponding salts of the other two acids at equivalent concentration. This can scarcely be due to calcium methoxypropionate being much less dissociated than the other two calcium salts, for, to judge from methoxy- and ethoxy-acetic acids, methoxypropionic acid ought to be a stronger acid than its homologues. We must therefore conclude that even in the case of these alkyloxy-acids, there are other factors connected with the solvent, besides electrolytic dissociation, which influence the rotation. This is also borne out by our observations on sodium ethoxypropionate in alcoholic solution. Not only is the rotation greatly diminished, as we have already stated, but the increase on dilution is so great that we can scarcely conceive it to be due to electrolytic dissociation alone.

We intend to continue the investigation of alkyloxy-acids, and hope



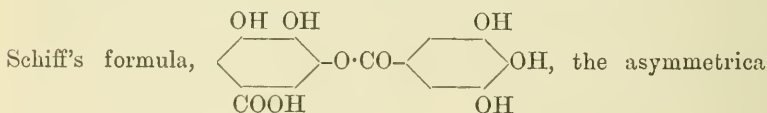
shortly to publish the results of observations on the dialkyloxysuccinic and alkyloxyphenylacetic acids, which we have already prepared and partly examined.

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## LXXXVII.—*The Optical Activity of Gallotannic Acid.*

By OTTO ROSENHEIM, Ph.D., and PHILIP SCHIDROWITZ, Ph.D.

SOME twenty-seven years ago, H. Schiff proposed a formula for gallotannic acid which was in accordance with all the then known properties of this substance, and it was, therefore, substantially accepted as correct. F. Günther's\* discovery, since confirmed by Schiff (*Chem. Zeit.*, 1895, 1860) and P. Walden (*Berichte*, 1897, 30, 151), that gallotannic acid is strongly dextrorotatory, has, however, put a different complexion on the question of its constitution, for in



carbon atom necessary to produce optical activity is absent. It must therefore be assumed either that Schiff's formula is incorrect, or that we are dealing with a substance which does not conform to the well-known law of van't Hoff and Le Bel. The latter possibility is hardly worthy of serious consideration, in face of the fact that every substance possessing optical activity—over 700 are now known and classified (Landolt, *Das optische Drehungsvermögen organischer Substanzen*, 2 Aufl.)—acts in strict accordance with that law, and that the apparent exceptions have, in every instance, been satisfactorily explained. Günther was, therefore, more than justified in suggesting that Schiff's formula must be wrong. Schiff (*Chem. Zeit.*, 1896, 865) is, however, of opinion that his original formula is more satisfactory than any other in explaining the chemical properties of this substance, but admits that for the present it is not possible to construct a ketone formula containing an asymmetrical carbon.

More recently, P. Walden (*loc. cit.*) has sought to explain this ab-

\* *Ber. pharm. ges.*, 1895, 5, 179, 297. *Centralblatt*, 1896, 1, 189. We note from an abstract in the *Chem. Zeit.*, 1898, 583, that F. M. Flavitzky claims to have first observed the optical activity of this substance.

normal position of gallotannic acid in relation to van't Hoff's theory, by showing that so-called 'pure gallotannic acid' is not pure, and he succeeded in separating the 'pure' gallotannic acid of commerce into several fractions possessing widely different rotatory powers.

The authors have made some investigations in this subject for two reasons.

1.—To ascertain whether a *homogeneous* gallotannic acid of *constant* rotatory power exists.

2.—To determine whether the optical properties of this substance might not be of use for analytical purposes.

As, for various reasons, we have been compelled to interrupt the work in this direction for the present, it seemed advisable to communicate the results obtained so far.

In the first place, a number of so-called 'pure' gallotannic acids have been examined, and we can entirely confirm the observations of Schiff and Walden as to the wide limits within which this rotation varies, the minimum observed for  $[\alpha]_D$  being  $+11^\circ$ , and the maximum  $+74.2^\circ$  (Schiff found from  $+14^\circ$  to  $+67^\circ$ , and Walden from  $+15^\circ$  to  $+67^\circ$ ). Further, on subjecting these same samples to various processes of purification, we were able to separate them into fractions whose rotatory powers varied from  $[\alpha]_D \pm 0^\circ$  to  $[\alpha]_D + 75.2^\circ$ . *The results obtained by the purification of the highest fractions, together with the quantitative examination of the yield in each case, have forced us to the conclusion that each of the samples investigated contains a homogeneous gallotannic acid possessing an optical activity of approximately  $[\alpha]_D + 75^\circ$ .* By employing the method described below, we obtained this substance from the commercial samples displaying the lowest, as well as the highest, optical activity, and it was not found possible, although many attempts by different methods were made, to split this up further into fractions differing in their optical value.

In order to obtain further proof of the uniform rotatory power of pure gallotannic acid, we prepared several derivatives of it, and subjected them to direct comparison with the same derivatives made from commercial gallotannic acids. It seemed obvious that, if all the commercial samples contained an appreciable quantity of a homogeneous substance, the purified derivatives would also be of equal rotatory power, and this would be identical with that of the derivative obtained from the pure gallotannic acid. In order to test this supposition, we prepared the quinine salts and the pentacetyl derivatives, both of which can be easily obtained from commercial gallotannic acids and from the purified product. It was found that the derivatives obtained from gallotannic acids of  $[\alpha]_D + 11^\circ$  up to  $[\alpha]_D + 75^\circ$  are identical in rotatory power *inter se*, and also with those prepared from the purified gallotannic acid.

We are inclined to regard the presence of varying amounts of gallic acid (which is inactive) in the commercial gallotannic acids as one of the causes determining the diversity of rotation.\* All the samples gave Young's tannic acid reaction, the depth of the colour being approximately in inverse ratio to the rotatory power. Gallotannic acid, highly purified by the authors' method, and having the highest rotation, was found to be quite free from gallic acid. Moreover, by mixing gallic acid with purified gallotannic acid, the rotation was reduced in direct proportion to the amount added. Crystallised (*perfectly inactive*) gallic acid was obtained in varying quantities from all the (*amorphous*) commercial gallotannic acids examined.

Gallic acid, however, is by no means the only substance causing the depression of the optical activity of gallotannic acid. It will be seen on referring to the succeeding paper that salts in general possess an enormous influence on the specific rotation. There is apparently a connection between the degree of alkalinity of the salt and its power of reducing the rotation, the ratio being direct. Very small quantities of different salts suffice to produce a great depression. The samples examined contained from 0.06 to 0.97 per cent. of mineral matter,† but as we know very little at present about this mineral matter, and more especially as we are in complete ignorance as to the nature of the acids, probably organic, with which it is combined, it is not possible to draw any definite conclusions. However, in the light of what we say further on with regard to the action of salts, it may be assumed that the mineral matter contained in commercial gallotannic acids does possess a similar influence. We have found that some samples contain an appreciable amount of zinc, probably due to the fact that the watery syrup of gallotannic acid obtained in the course of manufacture is frequently poured on to zinc plates to obtain the product in a light, flaky condition. Glycerol and oily substances are at times added for the same purpose, and may have some influence on the rotation of the finished article. It is possible also that resinous substances which were isolated in small quantities from all the samples, may have some modifying effect, and it may here be noted that an inactive substance was isolated from the commercial acid showing the lowest rotation ( $[\alpha]_D + 11^\circ$ ), which immediately became resinous on exposure to the air, and was certainly not gallic acid. Another factor influencing the rotation may, perhaps, be the presence of nitrogenous substances. All the samples examined contained nitrogen. Although

\* For the identification of gallic acid, we made use of Young's excellent reagent, namely, a solution of potassium cyanide, which gives a characteristic red coloration with the acid (*Chem. News*, 1883, 48, 134).

† Compare also M. Klar (*Pharm. Zeit.*, 1897, 12, 164), who asserts that 'pure' gallotannic acid leaves from 0.19 to 0.4 per cent. of ash.

the actual quantity was small, the nitrogenous matters represented thereby may be fairly large. We are at present unaware of the nature of these compounds, but if we remember that many amido-acids, &c., are optically active, it is not too much to assume that the presence of this nitrogenous matter may have some influence on the rotation.

### EXPERIMENTAL.

For the sake of clearness, we classify our results under the following three headings.

1.—Examination of various commercial gallotannic acids.

2.—The preparation of a homogeneous gallotannic acid of constant rotatory power.

3.—The specific rotation of some gallotannic acid derivatives prepared from pure and from commercial gallotannic acids.

I. The samples examined were obtained direct from different works and dealers as "chemically pure gallotannic acid." They all gave the characteristic gallic acid reaction, and contained varying amounts of water and ash. The results of the analytical\* examinations are tabulated below.

No.	Water.	Ash.	Nitrogen.	$[\alpha]_D^{25}$ †
I.	9.68 per cent.	0.06 per cent.	—	66.2
II.	7.34 "	0.97 "	—	13.0
III.	10.20 "	0.13 "	0.07 per cent.	12.0
IV.	10.77 "	0.09 "	0.04 "	36.6
V.	9.01 "	0.19 "	—	37.8
VI.	11.10 "	0.12 "	0.05 "	62.0
VII.	9.80 "	0.07 "	—	11.0
VIII.	9.11 "	0.07 "	—	41.6
IX.	9.51 "	0.20 "	—	23.1
X.	9.80 "	0.14 "	0.05 "	74.2

II. *Preparation of a Homogeneous Gallotannic Acid from Commercial Samples.*—Walden (*loc. cit.*) has shown that it is possible, by using

\* As no trustworthy quantitative method for separating gallic acid from gallotannic acid is known, we have made no attempt to estimate the former. Combustions of the substances in question are also of little value, as Löwe (*Zeit. anal. Chem.*, 11, 365) has already shown. He obtained practically the same figures from the commercial and the highly purified products.

† The optical measurements were made in a Laurent instrument (Schmitt and Haensch), mostly in a 200 mm. tube. The substances examined were all dried to constant weight in a vacuum. The readings apply to a 1 per cent. solution at 15°. Five readings were made in each case and the average taken.

different methods of purification, to obtain from a sample of commercial gallotannic acid products differing in rotatory power. The authors deemed it probable that, by continued purification of the fraction displaying the highest rotation, which is also the largest in amount, a gallotannic acid of uniform rotatory power might be obtained. If gallic acid be regarded as the chief impurity, it is in the first place necessary to find a solvent which will readily dissolve gallic acid, and from which gallotannic acid alone may be precipitated in as high a state of purity as possible. As there is nothing very definite in literature in regard to the solubility of gallic acid in the various solvents feasible for this purpose, the authors have made a series of determinations, the results of which are as follows.

*Solubility of Gallic Acid in various Solvents at 15°.*

100 parts dissolve	Gallic acid.	100 parts dissolve	Gallic acid.
	Per cent.		Per cent.
Acetone (dry).....	29.4	Chloroform .....	—
Acetone + 5 per cent. H <sub>2</sub> O...	22.2	Benzene and ethylic acetate	
Alcohol absolute .....	22.2	(1 : 1).....	0.77
Alcohol 90 per cent.....	18.9	Ether (dry) .....	2.5
Ethylic acetate (dry).....	8.4	Ether (moist) .....	2.7
Ethylic acetate (saturated		Chloride of sodium (26.9 per	
with H <sub>2</sub> O) .....	6.2	cent.).....	0.96
Benzene .....	—	Water (at 12.5° C.).....	0.76

It will be seen that acetone is the best solvent for the acid. Gallotannic acid also dissolves with the greatest ease in acetone, and it was to be expected, therefore, that the latter would be obtained in a fairly pure state from the dissolved mixture, if some means could be found to precipitate it whilst leaving the gallic acid in solution. This result was obtained in the following manner. On adding ether to the acetone solution, an amorphous precipitate was formed in most cases, which became resinous on exposure to the air. To the filtrate, a little water was then added, when two layers were formed, and on removing the supernatant ethereal layer and repeatedly shaking the heavier layer with ether until the latter remained colourless, most of the residual soluble impurities and colouring matters were extracted. On adding a little more water, three layers were formed, of which the lowest was a syrupy, concentrated solution of gallotannic acid containing a small quantity of ether; the middle one, an acetone solution rich in gallic acid, with a little gallotannic acid, the upper layer being an ethereal solution containing small quantities of gallic and gallotannic acids.



The lowest layer was separated, the ether removed on the water bath after adding a little water, and the syrupy residue dried in a vacuum in the dark. In the majority of cases, the product thus obtained gave the gallic acid reaction in a very slight degree only, and on repeating the above process several times, this no longer appeared. In proportion as the gallic acid reaction became weaker, the rotatory power of the product increased.

It was found that gallotannic acids of the most divergent original optical activity (from  $[\alpha]_D + 12^\circ$  up to  $[\alpha]_D + 66.2^\circ$  and  $+ 74.2^\circ$ ), when treated in the manner described, all yielded a substance of uniform rotatory power  $[\alpha]_D + 75^\circ$  to  $[\alpha]_D + 75.2^\circ$ . The yield of this homogeneous product varied in accordance with the original rotation from 50—75 per cent., calculated on the raw material. Besides this, 5 to 7 per cent. of fractions of medium rotation, and 2 to 7 per cent. of inactive, crystallised gallic acid were obtained. The fact that Walden did not succeed in isolating a gallotannic acid having a uniform specific rotation, but only fractions varying in optical activity, must be ascribed to the methods of purification he employed. He made use of solvents and precipitants which do not permit of the separation of gallic acid from gallotannic acid. Apart from this, some of the methods used doubtlessly tend to enrich the (supposedly) purified product with salts, which cannot fail to exert an action on the rotatory power.

3. *The Optical Activity of some Gallotannic Acid Derivatives.*—The authors desired, apart from the preparation of the substance as such, to have further proof of the existence of a definite gallotannic acid in the commercial product. For this purpose (as already mentioned in the introduction), we prepared the acetyl\* and quinine† derivatives, which are practically insoluble in water. Acetylgallic acid is soluble in dilute sodium carbonate solution and quinine gallate in water, and it is therefore not difficult to obtain a complete separation of these substances, as well as of the mineral matter, from the insoluble gallotannates. It will be seen from the table below that the rotatory powers of the derivatives obtained from the most highly purified gallotannic acid as well as from commercial samples are identical for the same solvent. It may be concluded, therefore, that all the crude products contain one and the same parent substance.

\* The acetyl derivatives were prepared from the various samples according to Schiff's method (*Annalen*, 1873, 170, 72) by boiling the acid with acetic anhydride, pouring the solution obtained into water, treating the precipitate with soda and then recrystallising from alcohol. The melting points of the derivatives from the various samples were identical.

† The quinine salts were prepared by Henry's method, which yields products of a homogeneous character. They were further purified by precipitating the alcoholic solution repeatedly with water.

*Specific Rotation  $[\alpha]_D$  of Acetylgallotannic Acid.  $c = 1$ ;  $t = 15^\circ$ .*

Number.	Rotation of the original gallotannic acid.	Rotation of the acetyl derivative in				
		Acetone.	Chloroform.	Ethylic acetate.	Acetic acid.	Acetic acid and alcohol (1:1).
V. ....	+37.8°	+10°	+5.4°	+10°	—	+16.6°
III. ....	+12	+10	+5.2	+10	+10°	+16.6
X. ....	+74.2	+10	+5.0	+10	+10	+16.6
Purified with acetone ...	+75.2	+10	+5.0	+10	—	+16.6

Schiff states that the rotation of an acetyl derivative obtained from a gallotannic acid of  $[\alpha]_D + 67^\circ$  in a mixture of alcohol and acetic acid is  $[\alpha]_D + 17^\circ$ .

*Rotation of Quinine Gallotannate in Methylic Alcohol.  $c = 0.5$ ;  $t = 15^\circ$ .*

Number.	Original gallotannic acid $[\alpha]_D$ for water.	Quinine tannate $[\alpha]_D$ for methylic alcohol.
I. ....	+66.2°	-40.1°
III. ....	+12	-40.1
VII. ....	+11	-39.4
Purified with acetone..	+75.2	-40.1

The authors found methylic alcohol to be the most suitable solvent for the somewhat insoluble quinine gallotannate. The solutions were made by dissolving the salts in hot methylic alcohol, cooling and making up at  $15^\circ$ , and if necessary filtering. The slight discrepancy shown by No. VII. is undoubtedly due to the fact that it is somewhat difficult to obtain the tannates in an absolutely homogeneous state.

The results enumerated above lead us to draw the following conclusions.

I. Commercial, so called 'pure' gallotannic acid contains varying quantities of gallic acid and mineral substances to which the great difference in optical activity, ranging from  $[\alpha]_D + 11^\circ$  to  $[\alpha]_D + 74.2^\circ$ , is probably due.

II. The chief constituent of all these commercial products, however, is a substance which has (as nearly as possible) a value of  $[\alpha]_D + 75^\circ$ .

III. The acetyl derivatives and quinine salts prepared from crude samples of gallotannic acid of specific rotation  $[\alpha]_D + 11^\circ$  to  $[\alpha]_D + 74.2^\circ$  possess identical rotatory powers for the same solvent.

IV. Schiff's formula contains no asymmetrical carbon, and is, therefore, not a correct representation of the constitution of this substance.

### LXXXVIII.—*The Influences Modifying the Specific Rotatory Power of Gallotannic Acid.*

By OTTO ROSENHEIM, Ph.D., and PHILIP SCHIDROWITZ, Ph.D.

THE specific rotatory power of an optically active substance in solution for a given ray of light is by no means a definite and fixed number, but, in the majority of cases, depends to a greater or less extent on the following conditions.

1. The temperature of the solution. 2. The concentration of the solution. 3. The nature of the solvent. 4. The action of optically inactive substances (salts, &c.).

It appeared of interest to the authors to study the influences modifying the specific rotation of gallotannic acid, for various reasons, and, among others, in order, if possible, to obtain some explanation of the great differences in optical properties displayed by the various commercial 'pure' gallotannic acids described in the preceding paper. The gross percentage of impurity in these samples being insufficient to account for the very low rotations of some of the samples, it was, therefore, probable that they contained salts or other substances which *specifically* affected the rotatory power. It may be stated at once that the authors have not yet succeeded in identifying, as such, the substances which exercise this modifying influence; but it must be remembered that the percentage of mineral matter in the various substances is very small, and that the nature of the, no doubt chiefly organic, acids with which this mineral matter is originally combined is practically unknown. The object of the present paper was rather in the nature of a preliminary investigation of the various influences which may affect the specific rotatory power of gallotannic acid, and thus, eventually, to throw some light on the actual causes.

The authors have examined the changes produced in the specific rotatory power of gallotannic acid in regard to 2, 3, and 4 (see above), but have, for the sake of simplicity, eliminated the influence of temperature by conducting all the experiments at  $15^\circ$ . The material employed was the apparently homogeneous product of the constant specific rotation  $[\alpha]_D^{15} + 75.2^\circ$  described in the preceding paper.

### *Influence of Concentration.*

Biot (*Mém. de l'Acad.*, 15, 93) first showed the dependence of specific rotation on the concentration of the solution, in the case of aqueous solutions of tartaric acid. Since then, numerous\* investigations in this direction, with interesting results, have been carried out on a great number of substances.

*The Influence of Concentration on the Specific Rotatory Power of Gallotannic Acid.*—The authors have found that, in aqueous solutions containing up to 1 per cent., it appears that the rotation is constant at  $[\alpha]_D^{15} + 75.2^\circ$ . By increasing the concentration beyond this figure, the optical activity is *decreased*, but the numbers obtained cannot be considered very accurate, on account of the rapid deepening of the yellow colour of the solution, which, in fact, makes readings above 10 per cent., even in a 100 mm. tube, quite impossible (compare Schiff, *Chem. Ru. Zeit.*, 1895, p. 1680). The subjoined table shows the actual influence of concentration as far as it has been capable of determination by the authors.†

TABLE I.—*Influence of Concentration on the Specific Rotatory Power of Gallotannic Acid in Aqueous Solution.*

Strength of solution per cent.	$[\alpha]_D^{15}$	Strength of solution per cent.	$[\alpha]_D^{15}$
10	+66.1°‡	1.0	+75.2°
5	+71.8 ‡	0.5	+75.2
2.5	+75.0	0.25	+75.2

### *Influence of the Solvent.*

Relatively complete investigations on the influence of the solvent on rotation generally are by no means so numerous as those on concentration, and are, broadly speaking, restricted to dextrotartaric acid (Landolt, *Ber.*, 1880, 13, 2332; Příbram, *Ber.*, 1889, 22, 6); three substituted ethereal salts of tartaric acid (Freundler, *Compt. rend.*, 1893, 117, 556; *Ann. chim. phys.*, 1895, [vii], 4, 244); camphor (H. Vogel, *Dissert. Berlin*, 1892); American turpentine (Landolt,

\* For a full account, see Landolt, "*Das optische Drehungsvermögen*," 1898, pp. 146—148.

† The instrument used in all our work was a half-shadow Schmidt and Haensch polarimeter, five readings being made in each case and the mean taken.

‡ In 100 mm. tube, the other readings in 200 mm. tube.

*Annalen*, 1877, 189, 311, &c.), and saccharose (Tollens, *Ber.*, 1880, 13, 2303).

The authors have examined the influence of various solvents on the rotatory power of gallotannic acid, and have found that the optical activity of this substance depends to a very marked extent on the nature of the solvent. Thus the original specific rotation  $[\alpha]_D^{15} + 75.2^\circ$  (for water) is actually reduced to  $\pm 0^\circ$  for a mixture of acetone and carbon tetrachloride, and acetone alone produces a remarkable fall. This is of considerable interest, as, so far as the authors are aware, there is only one other substance that is affected to anything like the same degree by this solvent, namely, dextrotartaric acid, the rotation of which is reduced from  $+14.40^\circ$  for water to  $\pm 0^\circ$  for a mixture of acetone and ether. It will be seen on referring to Table II that mixtures of acetone with ether, benzene, chloroform or ethylic acetate, as well as alcohol, ethylic acetate, and ethylic acetoacetate by themselves have a very powerful effect.

TABLE II.—*Influence of the Solvent on the Specific Rotation of Gallotannic Acid.*

(Strength of solution = 1 per cent.)

Solvent.	$[\alpha]_D^{15}$	Solvent.	$[\alpha]_D^{15}$
1. Water .....	+75.2°	6. 50 per cent. acetone + 50	+16.6°
2. Alcohol .....	+15.0	per cent. benzene .....	
3. Acetone .....	+11.6	7. 50 per cent. acetone + 50	+14.3
4. 50 per cent. acetone + 50	+11.6	per cent. chloroform....	
per cent. ether .....		8. Ethylic acetate .....	+8.3
5. 50 per cent. acetone + 50	+12.3	9. Ethylic acetoacetate .....	+12.6
per cent. ethylic aceto-		10. 80 per cent. acetone + 20	$\pm 0$
acetate .....		per cent. CCl <sub>4</sub> .....	

In reference to this section, it may be stated that, although none of the solvents examined produced a change of sign (as is the case, for instance, with dextrotartaric acid),\* yet the gross effect produced is greater with gallotannic acid than in the case of any other substance that has formed the subject of similar investigations.

*Action of Optically Inactive Substances.*

Experiments, chiefly with tartaric acid (Biot, *Mem. del' Acad.*, 1838, 16, 229; and *Ann chim. phys.*, 1844, [iii], 11, 82; Koch, *Dissert. Tübingen*,

\* From  $+14.4^\circ$  for water to  $-8.09^\circ$  for monochlorobenzene.



1869 ; Gernez, *Compt. rend.*, 1887, 104, 283, &c.) ; the tartrates (Long, *Sill. Americ. J.*, 1888, [iii], 36, 351 ; Schütt, *Ber.*, 1888, 21, 2586) ; malic acid (Gernez, *Compt. rend.*, 1889, 109, 151 and 769, &c.) ; and the sugars (E. v. Lippmann, *Die Chemie der Zuckerarten*, pp. 673—681 ; Farnsteiner, *Ber.*, 1890, 23, 3570, &c.), have shown that the addition of various inactive substances to a solution of an active compound exercises a more or less important influence on its rotatory power. Work in this direction has so far been practically confined to the substances mentioned above, a fact which appears at first sight somewhat remarkable considering the importance of the matter, both from a scientific and practical point of view. We have found in gallo-tannic acid a substance the optical properties of which are influenced to a remarkable degree by the presence of certain inactive compounds. For the sake of convenience we have classified these inactive substances into three groups, namely,

*a.* Acids ;                      *b.* Bases ;                      *c.* Salts.

*a.* There does not appear to be any detailed account, in literature, of the action of acids on rotation generally, but the addition of boric acid to tartaric acid solutions causes a very great rise (from  $[\alpha]_D + 12.88^\circ$  for a 16.63 per cent. solution to  $[\alpha]_D + 43.44^\circ$  for the same solution with 1 molecule of boric acid (Biot and Koch, *loc. cit.*).

The authors have found that mineral acids and boric acid have no influence on the specific rotation of gallotannic acid, but, on the contrary, restore the same to the normal if added to a solution, the optical properties of which have been previously depressed by the addition of alkalis or alkaline salts in small quantities. Thus the addition of concentrated hydrochloric acid up to 10 per cent., and of sulphuric acid to the point of precipitation, produced no effects whatever. Acetic acid exercises a depressing influence, but this is probably due to partial acetylation. A 10 per cent. aqueous solution of gallotannic acid (originally  $[\alpha]_D^{15} + 75.2^\circ$ ) containing 25 per cent. acetic acid has  $[\alpha]_D^{15} + 65.0^\circ$ . A similar solution containing 50 per cent. acetic acid shows  $[\alpha]_D^{15} + 36.6^\circ$ .

In view of the fact that gallic acid is one of the chief impurities in commercial gallotannic acid, it is of interest to note that this substance does not specifically affect the rotation of gallotannic acid, but only (as will be seen from the subjoined tables) reduces the same in direct proportion to the quantity present in any particular mixture.

*Influence of Gallic Acid on the Specific Rotation of Gallotannic Acid.*

*a. Specific Influence.*—To 1 c.c. of a 20 per cent. solution of gallotannic acid ( $[\alpha]_{\text{D}}^{15^\circ} + 75.2^\circ$ ) varying quantities of gallic acid were added, the whole made up at  $15^\circ$  to 20 c.c., and polarised in a 200 mm. tube.

TABLE IIIa.

Quantity of gallic acid.	Percentage of gallic acid in solution.	$[\alpha]_{\text{D}}^{15^\circ}$	Quantity of gallic acid.	Percentage of gallic acid in solution.	$[\alpha]_{\text{D}}^{15^\circ}$
0.019 gram.	0.05	$75.2^\circ$	0.2 gram.	1.0	$75.2^\circ$
0.05 „	0.25	„	0.4 „	2.0	„
0.1 „	0.5	„	2.0 „	10.0	„

TABLE IIIb.—*Influence of Decreasing Percentage of Gallotannic Acid in Solution.*

Quantities in 20 c.c. of solution.		Percentages in solution.		$[\alpha]_{\text{D}_{\text{gt}+\text{g}}}^{15^\circ}$	$[\alpha]_{\text{D}_{\text{gt}}}^{15^\circ}$
Gallotannic acid.	Gallic acid.	Gallotannic acid.	Gallic acid.		
0.18 gram.	0.02 gram.	90	10	$67.5^\circ$	$75.0^\circ$
0.16 „	0.04 „	80	20	$60.0$	„
0.10 „	0.10 „	50	50	$37.5$	„
0.08 „	0.12 „	40	60	$30.0$	„

NOTE.— $[\alpha]_{\text{D}_{\text{gt}+\text{g}}}^{15^\circ}$  = Specific rotation of mixture.  $[\alpha]_{\text{D}_{\text{gt}}}^{15^\circ}$  = Specific rotation of gallotannic acid alone, as calculated from  $\text{gt} + \text{g}$ .

*b.*—E. von Lippmann (*loc. cit.*) has described the influence of the alkalis and alkaline earths on cane-sugar, and found that they decrease the rotation. Apart from this, the description of the action of alkalis and bases generally on optically active substances, in literature, is very meagre. We have found that the behaviour of ammonia in relation to the specific rotation of gallotannic acid is in striking contrast to the inactivity of acids, in fact, it exercises a very powerful specific action. On adding 5 or 6 drops of ammonia to a 1 per cent. solution of gallotannic acid ( $[\alpha]_{\text{D}}^{15^\circ} + 75.2^\circ$ ), *total inactivity* is immediately pro-

duced. If more ammonia be added, the colour of the solution becomes a dark yellow, which makes further readings impossible. The action of the caustic alkalis could not be studied at all, owing to the fact that the addition of even very small quantities rendered the solutions so dark in colour as to be too opaque for polarimetric measurements.

c. *The Action of Salts*.—The influence of salts on specific rotation has been fairly exhaustively studied in the cases of tartaric acid, the tartrates, malic acid, and the sugar (see pp. 887—8). Speaking broadly, the influence is slight if we except the extraordinary action of the molybdates, tungstates, and uranium derivatives. For example, Gernez (*loc. cit.*) has shown that the addition of ammonium molybdate to a solution of tartaric acid, in the proportion of 1 mol. of the former to 18 of the latter, increases the rotation no less than 60-fold. Walden (*Ber.*, 1897, 29, 2889) has recently made similar observations in regard to the influence of an alkaline uranyl nitrate solution on the rotation of malic acid, the increase being upwards of 500-fold. The influence of borax on the members of the mannitol group is also considerable (Landolt, *loc. cit.*), but apart from these examples the action of salts generally is, as we have already stated, slight, relatively large quantities producing only small effects.

The authors have found, however, that salts generally exercise a very great influence on the specific rotation of gallotannic acid. In many cases, a very small proportion of the salt suffices to produce a very considerable effect, and it seems more than probable that the extremely low rotations of some of the commercial samples mentioned in the preceding paper are due to the presence of small quantities of inactive salts which exercise a powerful specific action.

All the salts examined by us have a *depressing* action, the rotation decreasing up to a certain point as the percentage of added salt increases. This point forms, in the majority of cases, a *minimum*, and the further addition of salt causes a rise. This minimum varies according to the nature of the salt in question, as also does the quantity of salt necessary to produce the same, and the character of the subsequent rise. There is, however, apparently, a connection between the molecular weight of the salt and this minimum of rotation; *that is to say, the molecular rotation of the mixture of salt and gallotannic acid remains (within reasonable limits) fairly constant, and approximately equal to the molecular rotation of gallotannic acid alone.*

Thus, if  $x$  = the molecular weight of gallotannic acid,  $y$  = the molecular weight of salt,  $z$  = the minimum of rotation, then  $\frac{(x+y)z}{100} = M$ .

Within limits,  $M$  is found (considering all the circumstances) to be

a fairly constant number, approaching closely to the molecular rotation of gallotannic acid.

The following table gives the values of  $M$  for the various salts examined.

TABLE IV.—Values of  $M = \frac{(x+y)z}{100}$

Salt.	$[\alpha]_D^{15}$ minimum.	$x+y$	$M$
1. $W_4O_{13}Na_2 + 10H_2O$ .....	12.9°	1470	189.6
2. $Na_2B_4O_7 + 10H_2O$ .....	25.6	704	180.2
3. $K_2B_4O_7 + 5H_2O$ .....	26.3	646	169.8
4. $(NH_4)_2B_4O_7 + 4H_2O$ .....	26.5	586	155.3
5. $Li_2B_4O_7$ .....	28.3	492	139.2
6. $NaCl$ .....	68.0	380.5	258.7
7. $KCl$ .....	70.6	396.5	279.9
8. $NH_4Cl$ .....	71.1	375.5	266.9
9. $LiCl + H_2O$ .....	70.0	382.5	267.7
10. $NaHCO_3$ .....	54.0	406	219.2
11. $KHCO_3$ .....	56.3*	422	[265.8]
12. $Zn(CH_3COO)_2 + 3H_2O$ .....	68.5*	559	[382.9]
Gallotannic acid .....	75.2	322	242.1

\* Doubtful *minima*, the series interrupted owing to precipitation on further addition of the salt.

In order to study the influence of varying proportions of the above salts on gallotannic acid, the methods described under sodium tungstate (which exercises a more powerful action than any other salt examined) were in general employed. Modification of the general procedure was dependent on the solubility of the salt in question. It is needless to say that the salts used were all highly purified. It must also be remembered that the quantity of added salt was, in each case, limited by the precipitation of the gallotannic acid when a certain concentration was reached.

1. *Sodium tungstate*,  $W_4O_{13}Na_2 + 10H_2O$ .

*Solutions* I. 4 grams of purified gallotannic acid ( $[\alpha]_D^{15} + 75.2^\circ$ ) were dissolved in water to 20 c.c. (1 c.c. = 0.2 g.).

II. 4 grams of sodium tungstate were dissolved in water to 40 c.c. (1 c.c. = 0.1 g.).

III. 5 c.c. of II diluted with water to 100 c.c. (1 c.c. = 0.05 g.).

To 1 c.c. of solution I, varying amounts of II and III were added, the whole made up to 20 c.c.\* at  $15^\circ$ , and polarised at that temperature. The solutions of tungstate and gallotannic acid were all of a lemon-yellow colour, which became too deep for readings in the 200 mm. tube above 1 per cent. Nos. 6 and 7 were therefore determined in a 100 mm. tube. Above 4—5 per cent., a precipitate commenced to form.

\* The final solution therefore contained 1 per cent. of gallotannic acid; this strength was kept constant throughout.

TABLE V.—*The Influence of Sodium Tungstate on the Rotation of Gallotannic Acid.*

Quantities of III and II.	Weight of sodium tungstate in solution.	Percentage of sodium tungstate in solution.	$[\alpha]_D^{15^\circ}$
1. 0.5 c.c. III .....	0.0025 gram.	0.0125	69.2°
2. 2 c.c. III .....	0.01    "	0.05	62.2
3. 4 c.c. III .....	0.02    "	0.1	53.8
4. 1 c.c. II.....	0.1     "	0.5	24.6
5. 2 c.c. II.....	0.2     "	1.0	12.9
6. 4 c.c. II.....	0.4     "	2.0	13.5
7. 8 c.c. II.. .....	0.8     "	4.0	22.6

TABLE VI.

Percentage of salt dissolved.	Change of rotation for $[\alpha]_D^{15^\circ}$ .				
	$\text{Na}_2\text{B}_4\text{O}_7 + 10\text{H}_2\text{O}.$	$\text{K}_2\text{B}_4\text{O}_7 + 5\text{H}_2\text{O}.$	$(\text{NH}_4)_2\text{B}_4\text{O}_7 + 4\text{H}_2\text{O}.$	$\text{Li}_2\text{B}_4\text{O}_7.$	$\text{NaHCO}_3.$
0.01	73.5°	—	73.5°	74.5°*	72.6°
0.025	71.0	70.5°	70.9	—	—
0.05	66.8	68.8	68.0	64.6	66.3
0.1	61.3	60.1	64.6	64.5	62.1
0.25	56.5	—	57.0	—	—
0.5	45.3	49.3	50.0	49.3	58.0
1.0	26.0	40.0	41.6	28.3	54.0
2.0	25.6	26.3	26.5	29.8	54.2
3.0	27.6	—	—	—	—
4.0	28.6	—	26.5	—	54.2
5.0	—	26.3	26.5	—	—

\* The percentage in this case was 0.0125 and not 0.01.

Percentage of salt dissolved.	Change of rotation for $[\alpha]_D^{15^\circ}$ .					
	$\text{NaCl}.$	$\text{KCl}.$	$\text{NH}_4\text{Cl}.$	$\text{LiCl} + \text{H}_2\text{O}.$	$\text{KHCO}_3.$	$\text{Zn}(\text{CH}_3\text{COO})_2 + 3\text{H}_2\text{O}.$
0.01	73.6°	73.8°	72.8°	73.3°	73.0°	75.1°
0.05	71.1	72.2	71.8	72.1	68.6	73.5
0.1	68.0	70.6	71.5	70.1	64.8	68.5
0.2	70.5	72.2	71.1	70.0	—	—
0.5	72.0	73.1	72.8	72.6	56.3	—
1.0	—	73.3	73.3	72.8	—	—
2.5	72.6	—	—	—	—	—
5.0	73.5	75.5	74.5	73.1	—	—



The influence of ammonium molybdate and of uranium acetate was also examined, but owing to the deep coloration produced with the former and the precipitation caused by the latter, it was impossible to obtain readings.

#### NOTES TO TABLE VI.

It is interesting to note the marked influence of borax in contradistinction to boric acid, which has no effect. On neutralising carefully with mineral acids, the rotation was restored to the normal.

As is the case with other salts of an alkaline nature, the depression produced by sodium hydrogen carbonate is very considerable. It would be of interest to obtain readings for higher percentages of the salt, but this was found to be impracticable owing to the fact that above 4 per cent. the solutions become very dark coloured and reading difficult.

It was impossible to determine values for quantities of potassium hydrogen carbonate above 0.5 per cent., as on increasing the proportion of the salt precipitation of gallotannic acid occurred.

In the case of zinc acetate also, readings could not be obtained with more than 0.1 per cent. of the salt owing to precipitation of the metallic tannate, but it is clear that this acetate exercises considerable influence on the rotation.

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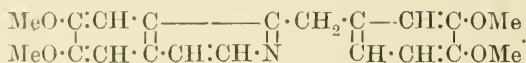
### LXXXIX.—*The Resolution of Tetrahydropapaverine into its Optically Active Components. Constitution of Papaverine.*

By WILLIAM JACKSON POPE and STANLEY JOHN PEACHEY.

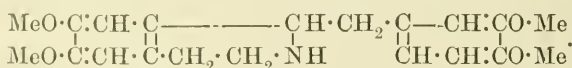
A STUDY of the literature referring to the natural alkaloids shows that valuable information respecting the constitution of some of these substances should result from an examination of the conditions under which carbon atoms in the molecule change from the asymmetric to the symmetric state, or *vice versa*, during the formation of simple derivatives; such information is of the greater value as being of a physico-chemical nature, and consequently different in kind from the evidence upon which constitutional formulæ are usually assigned to the more complex alkaloids. In the present paper, we deal with papaverine and its tetrahydro-derivative, showing that the latter contains an asymmetric carbon atom, as would be expected from the constitution attributed to it, and based on the results of its purely chemical examination. Since, at the outset of the work, the unsuitable character of the acid hitherto used for effecting the resolution of

racemic bases, namely, tartaric acid, became evident, we had to search for other acids more suitable for such purposes; these were found in the dextro- $\alpha$ -bromocamphorsulphonic acid and dextro- $\alpha$ -chlorocamphorsulphonic acid described by Kipping and Pope.

As one result of a large amount of laborious work on papaverine, G. Goldschmiedt succeeded in demonstrating (*Monats.*, 1888, 9, 778) that this alkaloid is very probably a tetramethoxybenzylisoquinoline having the following constitution.



Further, since on reducing isoquinoline derivatives, hydrogenation takes place first in the isoquinoline ring, the tetrahydropapaverine described by Goldschmiedt (*Monats.*, 1884, 7, 495) should have the constitution



These constitutional formulæ, although not actually proved, are probably correct, but any confirmatory evidence which can be adduced is naturally of value. In accordance with the optical inactivity of papaverine (*Monats.*, 1888, 9, 42), the constitution which Goldschmiedt assigned to it contains no asymmetric carbon atom, but during the conversion of this alkaloid into tetrahydropapaverine, that carbon atom of the isoquinoline ring to which the dimethoxybenzyl group is attached becomes asymmetric. Consequently, it is to be expected that tetrahydropapaverine is an externally compensated compound, and by applying suitable means it should be possible to resolve it into two enantiomorphously related components. We have succeeded in isolating dextro- and lævo-tetrahydropapaverine, and in demonstrating the racemic nature of the externally compensated base.

Up to the present time, only about a dozen or so externally compensated bases have been resolved into their optically active components by the crystallisation of the salts which they form with an optically active acid; and the only acid which has been used in effecting these separations is tartaric acid (Landolt, *Das optische Drehungsvermögen*, 1898, 97). A consideration of the cases in which tartaric acid has been used indicates that its use is attended with many disadvantages.

In the first place, tartaric acid has a far smaller dissociation constant, namely,  $\kappa = 0.097$ , than the mineral acids, hence it is to be expected that it would only form salts with powerful bases, and would not separate as a salt with feeble bases from solutions in hydroxylic solvents. The application of tartaric acid is thus very

limited, and all the externally compensated compounds which, hitherto, have been resolved into their active components by its aid are powerful bases. The use of a dibasic acid seems also inadvisable, because, in the crystallisation of the inactive base with the acid, neutral and acid salts may be formed, and so complicate the separation; this objection would not apply to a monobasic optically active acid. Further, a perusal of the work of Ladenburg shows that in many cases the dextrotartrate obtained from the racemic base is syrupy, and the mixture consequently difficult to separate.

Since separations by means of dextrotartaric acid are open to these and other objections, we decided to use an optically active acid to which such objections do not apply. Such acids are the dextro- $\alpha$ -bromo- and dextro- $\alpha$ -chloro-camphorsulphonic acids prepared by Kipping and Pope (*Trans.*, 1893, 63, 548); these acids are dissociated to an extent of over 90 per cent. in a solution of a gram-molecule in 30 litres (Walden, *Zeit. physikal. Chem.*, 1894, 15, 200), and so are comparable in strength with the mineral acids. These two sulphonic acids must, therefore, yield salts with very feeble bases; further, these sulphonic acids are monobasic, and their salts, as a rule, crystallise extremely well.

For the preparation of the optically active tetrahydropapaverines, crystallisation of the salts of the racemic base with dextro- $\alpha$ -bromocamphorsulphonic acid is found most convenient. Ammonium dextro- $\alpha$ -bromocamphorsulphonate, prepared by the last method given by Kipping and Pope (*Trans.*, 1895, 67, 356), is boiled in aqueous solution, in an open basin, with an excess of barium hydroxide until all the ammonia has been driven off, water being frequently added to replace that lost by evaporation; quantities of 50—100 grams of the ammonium salt are conveniently treated in one operation. The excess of baryta is now precipitated by passing a current of carbonic anhydride through the boiling solution, and, after filtering, the barium is removed from the solution of the barium salt by cautiously running dilute sulphuric acid from a burette into the hot solution. With care, a solution of dextro- $\alpha$ -bromocamphorsulphonic acid containing no barium and only a trace of sulphuric acid, can thus be readily obtained. The acid solution is now concentrated on the water bath to a convenient strength, and then titrated against standard alkali in order to determine how much dextro- $\alpha$ -bromocamphorsulphonic acid it contains.

This method of preparing the acid is more rapid and less costly than that involving the hydrolysis of the sulphonic chloride.

The papaverine used in the work was obtained from Merck of Darmstadt, and had the correct melting point, namely, 147—148°; it

was converted into the acid oxalate which crystallises well, and the salt was crystallised once from water. The oxalate was then dissolved in water, and the oxalic acid separated by means of calcium chloride; after filtering, a slight excess of ammonia was added and the precipitated papaverine collected, well washed with water, and dried in the air. The papaverine purified in this way melts at 147—148°, and is optically inactive in solution.

0.4024 gave 14.2 c.c. nitrogen at 14° and 755 mm.  $N = 4.17$  per cent.;  $C_{20}H_{21}NO_4$  requires 4.13 per cent.

*Racemic Tetrahydropapaverine.*

Papaverine was reduced by tin and hydrochloric acid in accordance with the method given by Goldschmiedt (*Monats.*, 1886, 7, 485), but the mechanical separation of the crystals of the hydrochlorides of papaverine and its reduction product was found to be unnecessary; no crystals of papaverine hydrochloride are contained in the product if the stannochloride be recrystallised several times from water before removing the tin by hydrogen sulphide. After purifying the hydrochloride by recrystallisation from boiling water, it is decomposed by adding excess of ammonia to its hot solution; as the solution cools, the tetrahydropapaverine separates in minute, glistening crystals. Goldschmiedt purified the base by crystallisation from water or dilute spirit, but we found it more convenient to prepare the acid oxalate; this salt is sparingly soluble in cold water, and after recrystallisation is treated with calcium chloride to remove the oxalic acid. The base is then precipitated by adding ammonia to the hot aqueous solution of its hydrochloride, collecting, washing well with water, and drying at 100°. Obtained in this way, it melts at 200—201°, and a solution of 2 grams made up to 25 c.c. with chloroform showed no rotation in a 200 mm. tube. The following analytical results were obtained.

I. 0.1364 gave 0.3495  $CO_2$  and 0.0905  $H_2O$ .  $C = 69.88$ ;  $H = 7.37$ .

II. 0.1429 „ 0.3659  $CO_2$  „ 0.0953  $H_2O$ .  $C = 69.84$ ;  $H = 7.41$ .

$C_{20}H_{25}NO_4$  requires  $C = 69.97$ ;  $H = 7.29$  per cent.

Crystals of racemic tetrahydropapaverine containing methylic alcohol of crystallisation have been recently measured by Koechlin (*Monats.*, 1898, 19, 321) who finds them to be tetragonal. On adding ammonia to a warm aqueous solution of the base in dilute hydrochloric acid and allowing it to cool, the base separates in microscopic crystals which are seen in the polarising microscope either as long needles having the ends cut off by a face at each end making a plane angle of 60° with the long side, or as needles with rectangular ends; the two kinds of crystals are apparently crystallographically identical,



the differences depending on how the crystals lie on the microscopic slide. The needles with oblique ends change colour on rotation between crossed Nicols, whilst those with rectangular ends extinguish straight; one optic axis of a biaxial interference figure is seen through the flat face of each kind of needle on conoscopic examination. The crystals are thus not tetragonal like those obtained from dilute alcoholic solution.

*Crystallisation of the Racemic Base with Dextro- $\alpha$ -bromocamphorsulphonic Acid.*

Racemic tetrahydropapaverine in quantities of about 10 grams is boiled with the calculated quantity of dextro- $\alpha$ -bromocamphorsulphonic acid dissolved in about 500 c.c. of water; solution of the base is facilitated by frequent addition of small quantities of ethylic alcohol. When the base is dissolved, the solution is filtered with the aid of the pump and allowed to cool, when long needles of lævotetrahydropapaverine dextro- $\alpha$ -bromocamphorsulphonate are deposited; these are washed with water, and the mother liquor and washings evaporated on the water bath, when a fresh crop of crystals is obtained. On continuing the evaporation of the mother liquors, the crystalline deposit becomes more and more contaminated with resinous dextro-tetrahydropapaverine dextro- $\alpha$ -bromocamphorsulphonate, and after a time this compound mainly separates; it forms a sticky deposit on the sides of the dish, which, on microscopic examination, is seen to contain a few doubly refracting needles of the lævotetrahydropapaverine salt. The crystalline salt is now submitted to fractional crystallisation from boiling water in order to free it as far as possible from the resinous salt.

*Lævotetrahydropapaverine Dextro- $\alpha$ -bromocamphorsulphonate,*



This salt is finally obtained, by crystallisation from its boiling aqueous solution, in long, flattened, colourless, transparent needles which melt at  $295\text{--}298^\circ$  (uncorr.) with frothing and evolution of gas; blackening sets in at about  $270^\circ$ . The crystals are very small, and complete crystallographic measurements could not be obtained. Six faces are present in the zone, of which the long edge of the crystals is the zone-axis; the angles from the large flat face in this zone are  $45^\circ 34'$  and  $93^\circ 44'$ , whilst the angle from the large flat face to one of the two faces which make the pointed end of the crystal is about  $82^\circ$ . The plane angle between the long edge and the edge between the large face and one of the end faces is about  $126^\circ 30'$ . A



very slight straight extinction is observable in the large face, the latter being nearly perpendicular to one optic axis of a biaxial substance; the optic axial dispersion is slight, the optic axial angle large, and the optic axial plane is nearly perpendicular to the long edge of the crystals.

The crystals do not lose weight at 100°, and give the following results on analysis.

- I. 0.1362 gave 0.2740 CO<sub>2</sub> and 0.0765 H<sub>2</sub>O.  
 II. 0.1458 „ 0.2935 CO<sub>2</sub> „ 0.0819 H<sub>2</sub>O.  
 III. 0.4117 „ 0.1189 AgBr and 0.1490 BaSO<sub>4</sub>.  
 IV. 0.4395 „ 0.1257 AgBr „ 0.1578 BaSO<sub>4</sub>.  
 V. 0.5173 „ 0.1471 AgBr.  
 VI. 1.2738 „ 22.8 c.c. of nitrogen at 14° and 762 mm.

	I.	II.	III.	IV.	V.	VI.	Theory for C <sub>30</sub> H <sub>40</sub> NBrSO <sub>3</sub> .
C .....	54.87	54.91	—	—	—	—	55.05 per cent.
H .....	6.24	6.24	—	—	—	—	6.12 „
Br .....	—	—	12.29	12.17	12.10	—	12.23 „
S .....	—	—	4.97	4.93	—	—	4.89 „
N .....	—	—	—	—	—	2.14	2.14 „

The salt is very sparingly soluble in cold water, but rather more soluble in absolute alcohol; it is practically insoluble in other ordinary organic solvents. A cold saturated solution in absolute alcohol was found to contain 0.2784 gram per 100 c.c. This solution in a 400 mm. tube gave

$$\alpha_D = -0^\circ 20' \text{ whence } [\alpha]_D = -30^\circ.$$

*Dextrotetrahydropapaverine Dextro- $\alpha$ -bromocamphorsulphonate,*  
 $C_{20}H_{25}NO_4 \cdot C_{10}H_{14}BrO \cdot SO_3H.$

This salt, when the sulphonate of the lævo-base has been separated as far as possible from it by crystallisation, is obtained, on evaporating the solution, as an almost colourless resin, which refuses to crystallise, even after being kept for a long time in the desiccator, and becomes constant in weight at 100°. We were unable, as will be seen from the behaviour of the base obtained from it, to free it wholly from the salt of the lævo-base.

*Lævotetrahydropapaverine,*  $C_{20}H_{25}NO_4.$

The base is prepared from purified lævotetrahydropapaverine dextro- $\alpha$ -bromocamphorsulphonate by dissolving the salt in much hot water, adding excess of ammonia, and allowing the solution to cool, when lævo-

tetrahydropapaverine separates in minute crystals. The lævo-base is very different in appearance from that of its racemic isomeride; the crystals of the latter, while in the mother liquor, appear much more transparent and granular than those of the optically active isomeride.

The crystals obtained by precipitating the hydrochloride with ammonia under conditions similar to those described when the racemic base was precipitated for microcrystallographic examination, seem to vary in kind with the temperature of precipitation. Sometimes the crystals are flattened pyramids on a square base, the side edges consisting of two lines containing a crystallographically small re-entrant angle; the extinction is straight with the sides, the optic axial plane is parallel to one side, a bisectrix of positive double refraction emerges in the centre of the field, and the optic axes emerge outside the field. Sometimes also the crystals of the lævo-base are minute, six-sided plates, the top faces of which are perpendicular to an acute bisectrix of negative double refraction; the optic axial angle is very small, and the crystals are often nearly uniaxial. Whether these two kinds of crystals are crystallographically identical and merely differ in orientation, or whether they contain different proportions of water of crystallisation, is not at present clear.

It is, however, evident that the crystals of the lævo-base are quite different crystallographically from those of the inactive base obtained under similar conditions; the inactive base is therefore racemic (Compare Kipping and Pope, *Trans.*, 1897, 71, 989.)

The base precipitated as above is colourless, and, after having been collected and well washed with cold water, is dried at  $110^{\circ}$ ; as freshly precipitated, it contains water of crystallisation and effloresces rapidly in the air. The base dried at  $110^{\circ}$ , melts sharply at  $223\text{--}224^{\circ}$  with previous discoloration. The following analyses refer to material dried at  $110^{\circ}$ .

- I. 0.1272 gave 0.3257  $\text{CO}_2$  and 0.0849  $\text{H}_2\text{O}$ . C = 69.83; H = 7.41.
  - II. 0.1384 „ 0.3548  $\text{CO}_2$  „ 0.0915  $\text{H}_2\text{O}$ . C = 69.91; H = 7.37.
  - III. 0.6218 „ 22.6 c.c. nitrogen at  $21^{\circ}$  and 767 mm. N = 4.27.
- $\text{C}_{20}\text{H}_{25}\text{NO}_4$  requires C = 69.97; H = 7.29; N = 4.08 per cent.

The following determinations of its specific rotation were made.

1.0008 gram, made up to 25 c.c. with chloroform and examined in a 200 mm. tube, gave  $\alpha_D = -11^{\circ} 29'$ , whence  $[\alpha]_D = -143.4^{\circ}$ .

1.0953 gram, made up to 25 c.c. with chloroform and examined in a 100 mm. tube, gave  $\alpha_D = -6^{\circ} 33'$ , whence  $[\alpha]_D = -149.5^{\circ}$ .

*Dextrotetrahydropapaverine*,  $C_{20}H_{25}NO_4$ .

The base separated by ammonia from the resinous dextrotetrahydropapaverine dextro- $\alpha$ -bromocamphorsulphonate varies in melting point from  $196^\circ$  to  $220^\circ$ , and evidently still contains the laevo-isomeride. To free it from this is not easy, because all the salts of the active bases which we have yet examined are more soluble than those of the corresponding racemic base. The crude dextro-base was converted into its acid oxalate, and the solution repeatedly evaporated, the racemic oxalate which separated being removed and the residue redissolved; since the racemic oxalate is but sparingly soluble in water, whilst the oxalate of the dextro-base is very soluble, a considerable amount of purification is thus effected. The oxalate of the dextro-base crystallises in large, colourless pyramids which effloresce in the air; the base separated from it by treatment first with calcium chloride and then with ammonium hydroxide, is indistinguishable from levotetrahydropapaverine. After drying, it melts at  $223$ — $224^\circ$  with previous discoloration, and gave the following analytical results.

I. 0.1275 gave 0.3272  $CO_2$  and 0.0847  $H_2O$ .  $C = 69.98$ ;  $H = 7.38$ .

II. 0.1355 „ 0.3471  $CO_2$  „ 0.0908  $H_2O$ .  $C = 69.86$ ;  $H = 7.45$ .

$C_{20}H_{25}NO_4$  requires  $C = 69.97$ ;  $H = 7.29$  per cent.

1.0844 gram of the base, dried at  $110^\circ$ , made up to 25 c.c. with chloroform, and examined in a 100 mm. tube, gave  $\alpha_D = +6^\circ 40'$ , whence  $[\alpha]_D = +153.7^\circ$ .

1.0005 grams of the base, dried at  $110^\circ$ , made up to 25 c.c. with glacial acetic acid and examined in a 100 mm. tube, gave  $\alpha_D = +7^\circ 56'$ , whence  $[\alpha]_D = +198.3^\circ$ .

The crystallographic properties of the dextro-base are indistinguishable from those of the laevo-base, and the qualitative behaviour of both towards solvents is similar to that of racemic tetrahydropapaverine. On precipitating with ammonia a solution in which equal weights of the dextro- and laevo-tetrahydropapaverines have been dissolved, the racemic base melting at  $200$ — $201^\circ$  is obtained.

A scrutiny of the specific rotations of the two active bases shows discrepancies indicating that the methods of purification adopted are not quite satisfactory. This matter is still under investigation.

*Separation of the Optically Active Tetrahydropapaverines by means of Dextro- $\alpha$ -chlorocamphorsulphonic Acid.*

A titrated solution of dextro- $\alpha$ -chlorocamphorsulphonic acid prepared from the ammonium salt in the same way as the solution of

the bromo-acid may also be used for the resolution of racemic tetrahydropapaverine; its use, however, offers no advantages over that of the bromo-acid, and the separation seems a little more difficult to effect owing to lævotetrahydropapaverine dextro- $\alpha$ -chlorocamphorsulphonate crystallising rather less satisfactorily than the bromocamphorsulphonate. As was to be expected, the separation proceeds similarly in the two cases, and a separate description of the resolution by means of the chloro-acid is unnecessary.

*Lævotetrahydropapaverine Dextro- $\alpha$ -chlorocamphorsulphonate,*  
 $C_{20}H_{25}NO_4 \cdot C_{10}H_{14}ClO \cdot SO_3H$ .

This salt is the first to separate on crystallising racemic tetrahydropapaverine with the requisite amount of dextro- $\alpha$ -chlorocamphorsulphonic acid. After recrystallisation from boiling water, it is obtained in long, colourless needles indistinguishable in appearance from the crystals of lævotetrahydropapaverine dextro- $\alpha$ -bromocamphorsulphonate described above; it melts at 300—305° with profound decomposition, and darkens at 270°. The following analytical results were obtained.

- I. 0.1469 gave 0.3169  $CO_2$  and 0.0876  $H_2O$ .  
 II. 0.1522 „ 0.3288  $CO_2$  „ 0.0915  $H_2O$ .  
 III. 0.5890 „ 0.1415  $AgCl$  „ 0.2196  $BaSO_4$ .  
 VI. 0.5779 „ 0.1379  $AgCl$  „ 0.2175  $BaSO_4$ .

	I.	II.	III.	IV.	Theory for $C_{30}H_{40}NClSO_8$ 59.07 per cent.
C .....	58.83	58.91	—	—	59.07
H.....	6.63	6.68	—	—	6.56 „
Cl.....	—	—	5.93	5.89	5.81 „
S .....	—	—	5.12	5.17	5.25 „

Microcrystallographic examination shows that the crystals are isomorphous with those of lævotetrahydropapaverine dextro- $\alpha$ -bromocamphorsulphonate; the large face of the needles, however, shows a distinct nearly straight extinction, the optic axis emerging less nearly perpendicular to the face than in the crystals of lævotetrahydropapaverine dextro- $\alpha$ -bromocamphorsulphonate. A bisectrix of positive double refraction emerges through the large face.

The resinous dextrotetrahydropapaverine dextro- $\alpha$ -chlorocamphorsulphonate remaining in the mother liquors was not further examined.

*Lævotetrahydropapaverine from Lævotetrahydropapaverine Dextro- $\alpha$ -chlorocamphorsulphonate.*

On treating lævotetrahydropapaverine dextro- $\alpha$ -chlorocamphorsulphonate with ammonia, it yields the lævo-base just as does the lævo-

tetrahydropapaverine dextro- $\alpha$ -bromocamphorsulphonate. The base, after drying at 110°, forms a white powder melting at 223—224°.

*Attempts to resolve Racemic Tetrahydropapaverine by means of Reyhler's Camphorsulphonic Acid.*

The camphorsulphonic acid which Reyhler has recently prepared (*Bul. Soc. Chim.*, 1898, [iii], 19, 120) in so elegant a manner by the action of a mixture of acetic anhydride and sulphuric acid on camphor, is very easily obtained pure in large quantities; being a powerful monobasic optically active acid, it is naturally applicable to the resolution of racemic bases into their optically active components. When crystallised with racemic tetrahydropapaverine, however, it yields a syrupy mixture of very soluble salts which crystallise on standing. Since this acid is not so well adapted to the resolution of racemic tetrahydropapaverine as the acid of Kipping and Pope, its use in this particular case was abandoned.

—Instances in which this acid may be advantageously applied will be shortly published.

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XC.—*The Non-resolution of Racemic Tetrahydropapaverine by Tartaric Acid.*

By WILLIAM JACKSON POPE and STANLEY JOHN PEACHEY.

ON the publication of our note (*Proc.*, 1898, 122) announcing the racemic nature of tetrahydropapaverine and its resolution into optically active components, G. Goldschmiedt, who first prepared this base (*Monats.*, 1886, 7, 485), published a paper (*Monats.*, 1898, 19, 321) in which he stated that he has been occupied for several years on the same problem, and that, although he did not succeed in resolving the racemic base, he had prepared its dextrotartrate, determining its composition, and establishing many points of interest concerning the salt.

During the course of our work (see preceding paper), we prepared and carefully examined this salt, but the appearance of Goldschmiedt's paper renders the publication of much of our work on the subject superfluous. There are, however, several points about the compound which make it one of great interest.

Goldschmiedt states that racemic tetrahydropapaverine forms a single



salt with dextrotartaric acid of the composition  $(C_{20}H_{25}NO_4)_{1/2} \cdot C_4H_6O_6 + 17H_2O$ , and attributes his failure to resolve the base to the fact that this compound is a neutral salt, and that no acid salt could be prepared. We also were unable to prepare an acid dextrotartrate from the racemic base, and obtained the neutral salt which has the composition he assigned to it.

On allowing its hot aqueous solution to cool slowly, the tartrate crystallises in small, colourless, transparent prisms, which have a brilliant lustre and effloresce on exposure to the air. The crystals, which were examined in order to demonstrate that the salt is not a mixture, belong to the monosymmetric system, the dominant form being  $p\{110\}$  (Fig. 1); the next largest form observed is  $q\{011\}$  and the faces of this form give the best reflections of any on the crystals. The two pinacoids  $a\{100\}$  and  $b\{010\}$  are rarely observed and are always very small. It is difficult to obtain trustworthy measurements of these crystals, inasmuch as the faces are all rather distorted.

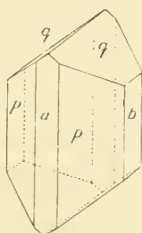
*Crystalline System.*—Monosymmetric.

$$a:b:c = 1.1464:1:0.7932$$

$$\beta = 82^\circ 30'$$

*Forms observed.*— $a\{100\}$ ,  $b\{010\}$ ,  $p\{110\}$ , and  $q\{011\}$ .

FIG. 1.



The following angular measurements were obtained.

Angle.	Number of measurements.	Limits.	Mean observed.	Calculated.
$ap = 100:110$	26	$47^\circ 38' - 49^\circ 41'$	$48^\circ 27'$	$48^\circ 39.5'$
$pp = 110:\bar{1}10$	42	$81^\circ 56' - 83^\circ 39'$	$82^\circ 41'$	—
$pp = 110:1\bar{1}0$	37	$96^\circ 12' - 97^\circ 1'$	$97^\circ 10'$	$97^\circ 19'$
$bp = 010:110$	16	$40^\circ 22' - 42^\circ 19'$	$41^\circ 12'$	$41^\circ 20.5'$
$bq = 010:011$	13	$50^\circ 48' - 52^\circ 35'$	$51^\circ 38'$	$51^\circ 49'$
$qq = 011:0\bar{1}1$	48	$75^\circ 14' - 77^\circ 36'$	$76^\circ 22'$	—
$qq = 011:01\bar{1}$	29	$102^\circ 40' - 104^\circ 52'$	$103^\circ 47'$	$103^\circ 38'$
$pq = 110:01\bar{1}$	24	$65^\circ 17' - 67^\circ 58'$	$66^\circ 39'$	—
$pq = 110:011$	9	$56^\circ 31' - 59^\circ 0'$	$57^\circ 14'$	$57^\circ 52'$

The crystals are very brittle and show no definite cleavage. On examination through  $p\{110\}$ , the extinction is seen to be very oblique to the long edge of the crystals, and one optic axis of a biaxial interference figure is observed emerging in the field.

Landolt (*Ber.*, 1873, 6, 1077) showed that the metallic tartrates have nearly the same molecular rotation, namely,  $[M]_D = +58.1^\circ$  to  $+64.6^\circ$ , in fairly dilute aqueous solution, so that the molecular rotation of the salt is nearly independent of the base which it contains. These results have been extended by Oudemans (*Annalen*, 1879, 197, 48, 66; 1881, 209, 38), Tykociner (*Rec. Trav. Chim.*, 1882, 1, 144) and others. It was therefore to be expected that the molecular rotation of racemic tetrahydropapaverine dextrotartrate would also have a value of about  $+60^\circ$ ; the sparing solubility of the salt renders the accurate determination of the molecular rotation difficult.

A solution of 0.9539 gram of the salt dried at  $100^\circ$ , made up to 100 c.c. with water, gave  $\alpha_D = +0^\circ 17'$  in a 400 mm. tube, whence  $[\alpha]_D = +7.43^\circ$  and  $[M]_D = +63.4^\circ$ .

A solution of 1.0069 grams of salt dried at  $100^\circ$ , made up to 100 c.c. with water, gave  $[\alpha]_D = +0^\circ 18'$  in a 400 mm. tube, whence  $[\alpha]_D = +7.45^\circ$  and  $[M]_D = +63.6^\circ$ .

A solution containing 1.1397 grams in 100 c.c. crystallised on cooling.

The mean values are  $[\alpha]_D = +7.44^\circ$  and  $[M]_D = +63.5^\circ$ , so that the molecular rotation is, within the limits of experimental error, of the same magnitude as those of the metallic tartrates.

After adding excess of ammonium hydroxide to the hot solution of the salt and allowing to cool, the base separates as minute, glistening needles which, after drying at  $110^\circ$ , melt at  $200-201^\circ$ ; a polarimetric examination of a chloroform solution containing 2 grams per 25 c.c. in a 200 mm. tube showed the base to be racemic tetrahydropapaverine.

Since we have previously demonstrated the racemic nature of inactive tetrahydropapaverine, it is obvious that the neutral tartrate contains a molecule each of the dextro- and lævo-base to each molecule of tartaric acid. The compound is therefore one of the kind which Ladenburg has recently discovered (*Ber.*, 1898, 31, 524) and described as "halbracemisch," a term which may be translated as "hemiracemic." The failure to resolve racemic tetrahydropapaverine by crystallisation with tartaric acid must be attributed to the occurrence of partial racemism, and not to the fact that the base does not yield an acid tartrate. There seems no *à priori* reason why a racemic base should not be resolvable by crystallising its neutral salt with an optically active acid as well as by crystallising its acid salt; in fact, we resolved the base by means of its neutral salts with dextro- $\alpha$ -bromocamphor-sulphonic acid.

Up to the present, the following partially racemic compounds have

been described namely, quinine racemic pyrotartrate (Ladenburg, *Ber.*, 1898, 31, 524, 937), and strychnine racemate (Ladenburg and Doctor, *Ber.*, 1898, 31, 1969).

Racemic tetrahydropapaverine dextrotartrate is thus the first partially racemic substance containing an externally compensated base which has been examined; it should, however, be mentioned that Ladenburg notes his inability (*Ber.*, 1894, 27, 75; 1898, 31, 524) to resolve inactive  $\beta$ -pipecoline by means of its bitartrate at the temperature of the water bath, owing apparently to the occurrence of partial racemism.

It must be concluded that if an inactive substance cannot be resolved into optically active compounds by crystallising its salts with an optically active base or acid, it is nevertheless still possible that the inactive compound is an externally compensated substance.

The authors desire to acknowledge their indebtedness to the Research Fund Committee of the Chemical Society for a grant enabling them to carry out the investigations described in these papers.

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## XCI.—*Composition of American Petroleum.*

By SYDNEY YOUNG, D.Sc., F.R.S.

IN 1895 (*Trans.* 1897, 71, 442), a successful attempt was made by the author, in conjunction with Mr. G. L. Thomas, to separate pure specimens of normal and iso-pentane from American petroleum, a combined dephlegmator and regulated temperature still-head being employed for the fractional distillation.

Earlier in the same year (*Proc.*, 1895-6, p. 172), a specimen of nearly pure normal hexane was obtained from "petroleum ether" by fractional distillation with a dephlegmator (*Chem. News*, 1895, 71, 177), with 12 columns, but even after treatment with a mixture of concentrated sulphuric and nitric acids, the hexane was slightly heavier (0.17 per cent.), than pure hexane from propyl iodide.

These results appeared sufficiently encouraging to warrant the anticipation that, by the fractional distillation of a larger quantity of the petroleum ether with the aid of the combined dephlegmator and regulated temperature still-head, after removal of benzene from the "ether" by treatment with mixed sulphuric and nitric acids, pure specimens of both normal and iso-hexane might be separated.

This expectation has not been fully realised, nor has it been found possible to obtain the heptanes in a pure state merely by fractional distillation. A comparison, however, of the results obtained in these

investigations with those of Markownikoff, Zelinsky and others, in their recent examination of Russian petroleum, and of Lachowicz in his study of Galician petroleum, appears to show that the same hydrocarbons are present in the oils from all these sources, and that the considerable differences in the specific gravity of fractions boiling within the same range of temperature are simply due to differences in the relative proportions of the three classes of hydrocarbons—paraffins, naphthenes, and aromatic compounds.

Evidence has, in fact, been obtained of the presence of the following hydrocarbons boiling between, say, 25° and 115°, in “petroleum ether” from American petroleum.

Name.	Boiling point 760 mm.	Remarks.
Isopentane .....	27·95°	{ Obtained quite pure by fractional distillation, after treatment with mixed sulphuric and nitric acids.
Normal pentane .....	36·3°	
Pentamethylene .....	About 50°	It is not improbable that other hexanes may be present in small quantity.
Isohexane .....	About 61°	
Normal hexane .....	68·95°	Quite pure by heating with fuming nitric acid after fractionation.
Methylpentamethylene .....	About 72°	Separated in nearly pure state by Miss E. C. Fortey, B.Sc.; pure from Galician petroleum.
Benzene .....	80·2°	
Hexamethylene .....	80·8°	
Isoheptane .....	90·3°	Other isomerides may be present. Doubtful.
? Dimethylpentamethylene ...	About 94°	
Normal heptane.....	98·4°	Nearly pure by bromination, fractionation of bromides, and reduction of heptylic bromide.
Methylhexamethylene .....	About 102°	
Toluene .....	110·8°	

It has been suggested by Markownikoff that trimethylene and tetramethylene and their homologues may be present in Russian petroleum, although no evidence has, so far as I know, been brought forward in support of this view. So far as American petroleum is concerned, there is evidence of the absence of tetramethylene and methyltetramethylene, for both normal and iso-pentane were obtained quite pure by fractional distillation, and this would not have been the case, at any rate without far greater difficulty than was actually experienced, if any other hydrocarbons had been present boiling between 20° and 45°. Now the boiling point of methyltetramethylene is given by W. H. Perkin, jun., as 39—42°, and that of tetramethylene itself would be about 20° lower.

*Isopentane and Normal Pentane.*

The separation of these paraffins has been fully described in the Transactions (1897, '71, 442), and a diagram of the apparatus employed is there given. Both substances were shown to be quite pure.

Lachowicz (*Annalen*, 1883, 220, 188) separated isopentane (b. p. 29—30°), and normal pentane (b. p. 37°), from Galician petroleum, and in the same year Mendeléeff showed that the fractions from 30° to 40° obtained by distilling Russian petroleum had the same specific gravity as similar fractions from Pennsylvanian petroleum. Aschan also separated isopentane from Baku petroleum (*Chem. Zeit.*, 1897, 21, 288).

*Pentamethylene.*

The comparatively small portion of the "petroleum ether" which boiled between 40° and 60° was subjected to fractional distillation with the combined dephlegmator and regulated temperature still-head, and it was found that a small quantity of liquid boiling at about 50° could be separated. The amount was, however, too small to allow of satisfactory results being obtained with the large apparatus, and, after 9 fractionations, the distillation was continued with the dephlegmator with 12 columns.

The boiling points—in all cases corrected to 760 mm.,—the weights of each distillate, the ratios of weight to temperature range, and the specific gravities of the best fractions are given below.

*After 9 fractionations with large apparatus.*

No. of fraction.	Boiling point.	Weight $\Delta w.$	$\frac{\Delta w}{\Delta t}$	Sp. gr. 0°/4°.
1	44·6 —48·7°	9·9 grams.	2·4 <sup>✓</sup>	not taken
2	48·7 —49·55	15·0 "	17·6	0·7014
3	49·55—49·9	16·8 "	48·0	0·7011
4	49·9 —51·05	16·8 "	14·6	0·7045
5	51·05—53·7	15·8 "	6·0	0·6919
6	53·7 —57·25	16·2 "	4·6	0·6836

*After 6 additional fractionations with dephlegmator.*

1	47·35—49·5°*	11·5 grams.	5·3	0·7029
2	49·5 —49·6	16·3 "	163·0	0·7035
3	49·6 —50·35	16·0 "	20·0	0·6975
4	50·35—56·4	15·0 "	2·5	not taken

\* Mostly above 49°.



The vapour density of fraction 2 (b. p.  $49.5-49.6^\circ$ ) was found to be 39.25 [calc. for  $C_5H_{10} = 35$ ; for  $C_6H_{14} = 43$ ] and corresponds roughly to an equal number of molecules of pentamethylene and hexane. The high specific gravity proves conclusively that a substance other than a paraffin is present, and the fact that a mixture of concentrated sulphuric and nitric acids has no action on it in the cold, points to its being a polymethylene hydrocarbon. Fuming nitric acid had no perceptible action on the liquid at the ordinary temperature, but when heated on the water bath until the hydrocarbon boiled vigorously, there was slow and regular action. No nitro-compound appeared to be formed for, after one day's heating, the acid gave no turbidity on dilution with water. On evaporating the diluted acid to dryness, however, a residue, consisting of oxalic, succinic, and glutaric acids, was left.

On heating with fairly dilute nitric acid at about  $150^\circ$  in sealed tubes for  $2\frac{1}{2}$  hours, a good deal of hydrocarbon disappeared, and the residue consisted of a mixture of a liquid nitro-compound and unaltered hydrocarbon (b. p.  $49.8-50.5^\circ$ ). The nitric acid, on evaporation, left a residue, consisting chiefly of glutaric acid, which, after purification, melted sharply at  $97.5-98^\circ$ , and gave a barium salt easily soluble in water, but precipitated by alcohol.

The quantity of nitro-compound was too small for satisfactory examination.

These results agree perfectly with those obtained by Markownikoff with Russian petroleum (*Annalen*, 1898, 301, 154). Two specimens of petroleum from different sources were fractionated by him with a Le Bel-Henninger dephlegmator, the fractions being collected at intervals of  $2^\circ$ . The quantity of liquid between  $40^\circ$  and  $50^\circ$  is only stated in one case but, from the context, it is clear that it was very small in both. The specific gravities at  $15^\circ/15^\circ$  are given in both cases, and it will be seen that there is a maximum at about  $50^\circ$ .

Temperature.	I.	II.	
	Sp. gr.	Sp. gr.	Weight.
46—48°	0.683	0.704	3 grams
48—50	0.689	0.718	24 „
50—52	0.691	0.716	51 „
52—54	0.686	0.700	19 „
54—56	0.678	0.668	7 „

Markownikoff purified his petroleum, before fractionation, by treatment with a mixture of sulphuric and nitric acids; by heating the 48—52° fractions with dilute nitric acid under pressure, he obtained

a nitro-compound and glutaric acid, and he obtained similar results with a specimen of pentamethylene (sp. gr.  $15^{\circ}/15^{\circ}=0.751$ ) prepared synthetically (*Ber.*, 1897, 30, 974).

*Isohexane (and Isomerides of lower Boiling Point?).*

The petroleum boiling from about  $56^{\circ}$  to  $72^{\circ}$ , after repeated treatment with a mixture of sulphuric and nitric acids, was fractionated with the combined dephlegmator and regulated temperature still-head.

As regards the portion boiling below  $65^{\circ}$ , it is evident that there is a considerable quantity of a hydrocarbon boiling at a temperature not far from  $60.5^{\circ}$ , presumably isohexane, and the low specific gravity shows that polymethylene compounds are absent or, at any rate, that their amount is inconsiderable. It was not, however, found possible to separate a liquid of absolutely constant boiling point and, indeed, no improvement is noticeable in the last six fractionations.

The results of the 11th and 17th fractionations are given below.

XI.				XVII.			
No. of fraction.	Temperature.	$\frac{\Delta w}{\Delta t}$	Sp. gr. $0^{\circ}/4^{\circ}$	No. of fraction.	Temperature.	$\frac{\Delta w}{\Delta t}$	Sp. gr. $0^{\circ}/4^{\circ}$
1	56.0 — 59.8°	75	0.6766	—	—	—	—
2	59.8 — 59.9	268	0.6745	2	59.9 — 60.05°	320	0.6738
3	59.9 — 60.3	306	0.6737	3	60.05 — 60.3	342	0.6733
4	60.3 — 60.6	551	0.6734	4	60.3 — 60.55	449	0.6729
5	60.6 — 60.85	790	0.6735	5	60.55 — 60.75	626	0.6728
6	60.85 — 61.15	541	—	6	60.75 — 61.0	500	0.6730
7	61.15 — 61.55	348	—	7	61.0 — 61.3	340	0.6738
8	61.55 — 62.05	308	0.6758	8	61.3 — 61.7	288	—
9	62.05 — 62.75	213	—	9	61.7 — 62.15	186	0.6762
10	62.75 — 63.75	149	—	10	62.15 — 62.65	200	—
11	63.75 — 65.0	52	0.6801	11	62.65 — 63.1	198	0.6792

It will be seen that, after the 17th fractionation, there is a minimum specific gravity and a maximum ratio of weight of distillate to temperature range ( $\Delta w/\Delta t$ ) in the 5th fraction. The variation of specific gravity with boiling point is very slight and, in this respect, the results resemble those with isohexane, but differ entirely from those obtained with the normal hexane and normal heptane fractions.

Comparing the 11th and 17th fractionations, the ratios  $\Delta w/\Delta t$  for fractions 2 and 3 show a moderate increase, but those for the higher ones a decrease.

If there were no other substance present, besides isohexane, with a boiling point between those of pentamethylene and normal hexane, there seems no reason why a progressive improvement should not take

place in the ratio  $\Delta w/\Delta t$  for the best fraction. If, on the other hand, an isomeric paraffin were present, with a boiling point not very different from that of isohexane, one would expect the ratios to increase up to a certain point while the mixture of isomeric hexanes was separating as a whole from the pentamethylene on the one hand, and the normal hexane on the other. Afterwards, the two isomeric hexanes would begin to separate from each other, and, if their boiling points were sufficiently far apart, the ratios  $\Delta w/\Delta t$  would, after a time, show two maxima, just as, in the separation of the pentanes from petroleum there was first a single maximum at about  $33^\circ$ , followed by a minimum at about this temperature and two maxima, one at  $28^\circ$  and the other at  $36.3^\circ$  (compare the curves, *Trans.*, 1897, 71, 444). But if their boiling points were very near together, the process of separation would be exceedingly slow and perhaps impossible to carry out completely, and the ratios  $\Delta w/\Delta t$  would then show but slight change.

The slight increase in the ratios for fractions 2 and 3 and the decrease for the higher fractions would seem to indicate the presence of a relatively small quantity of an isomeric hexane of somewhat lower boiling point than isohexane. Again, the fact that the liquid, consisting of a mixture of pentamethylene and a hexane, boiled nearly constantly at  $49.5^\circ$  makes it not improbable that a fourth isomeric hexane may be present in very small quantity.

During the present year, two papers have been published, one by Aschan (*Ber.*, 1898, 31, 1801), the other by Markownikoff (*Annalen*, 1898, 301, 154), in which it is stated that di-isopropyl (b. p.  $57-59^\circ$ , Aschan;  $58-62^\circ$ , Markownikoff) is present in Russian petroleum, and Markownikoff considers it probable that trimethylethylmethane is present in the fraction boiling at about  $47^\circ$ , and that other isomerides, isohexane, &c., may also be present in the fractions from  $58$  to  $64^\circ$ .

At present, the question, which of the hexanes, in addition to the normal and iso-compound, are present in American and Russian petroleum, cannot be regarded as settled, and it seems better to defer the further examination of American petroleum until pure specimens of the isomeric hexanes have been prepared synthetically. Lachowicz (*loc. cit.*) states that he separated isohexane (b. p.  $60-61^\circ$ ) from Galician petroleum.

#### *Normal Hexane.*

With regard to the hexane fractions, freed from benzene and boiling from  $65^\circ$  to, say,  $72^\circ$ , it was quite evident, after a few fractionations, that whilst normal hexane was present in large quantity, there was also another hydrocarbon, of much higher specific gravity, boiling a very few degrees higher. The researches of Markownikoff and Zelinsky made it probable that this substance might be methylpenta-

methylene, and that this polymethylene compound might be removed by heating the liquid with fuming nitric acid. Accordingly, after the fourteenth fractionation, each fraction was separately subjected to this treatment for five days, the acid—about equal in volume to the hydrocarbon—being removed and fresh acid added after the first and third days.

The result was satisfactory, and it was found that, not only was the methylpentamethylene removed by the nitric acid, but also the isohexane, a solid trinitrohexane being formed in considerable quantity. After treatment with the acid, the fractions were separately shaken with strong sulphuric acid several times, then with caustic soda, and finally with water. They were subsequently dried with phosphorus pentoxide, distilled over sodium wire, and fractionated several times with the 12-column dephlegmator to remove the last traces of dissolved nitro-compounds.

The results of the ninth and fourteenth fractionations, and of the final fractionation after treatment with nitric acid, are given in the table on page 912.

As the boiling point of pure normal hexane (from propylic iodide and sodium is  $68\cdot95^{\circ}$ \* and the sp. gr. at  $0^{\circ}/4^{\circ}$  is  $0\cdot67697$ , it will be seen that the five lowest fractions were quite pure, and that the three higher fractions contained only a very small amount of a heavier compound.

The critical temperature and pressure of fraction 3 were determined and the constants are compared below with those of normal hexane from propylic iodide. The vapour pressures and specific volumes at a few temperatures are also compared.

	Normal hexane from	
	Petroleum.	Propylic iodide.
Critical temperature .....	234·8	234·8°
„ pressure.....	22540	22510 mm.
Vapour pressure at 130° .....	3716	3719
„ „ 200 .....	13360	13349
„ „ 220 .....	18132	18100
„ „ 230 .....	20991	20955
Volume of a gram of liquid at 200° .....	2·297	2·291
„ „ „ 220 .....	2·627	2·625
„ „ „ 230 .....	3·019	3·004
Volume of a gram of saturated vapour at 200°...	15·88	15·75 to 15·90†
„ „ „ „ 220 ...	9·98	9·81 to 9·935
„ „ „ „ 230 ...	7·11	7·10 to 7·135

† By different methods.

\* Not  $69\cdot0$  as stated in a previous paper (Trans., 1895, 67, 1072).

IX.				XIV.				After treatment with nitric acid.		
No. of fraction.	Temperature.	$\frac{\Delta w}{\Delta t}$	Sp. gr. $0^{\circ}/4^{\circ}$	Temperature.	$\frac{\Delta w}{\Delta t}$	Sp. gr. $0^{\circ}/4^{\circ}$	Temperature.	W.	Sp. gr. $0^{\circ}/4^{\circ}$	
1	66.15—67.15°	88	0.6799	66.4 — 67.85°	55	0.6793	68.95°	24	0.67693	
2	67.15—68.0	133	—	67.85—68.35	102	—	”	39	0.67693	
3	68.0 — 68.5	243	—	68.35—68.7	237	—	”	59	0.67699	
4	68.5 — 68.8	427	0.6809	68.7 — 68.85	490	—	”	57	0.67697	
5	68.8 — 68.95	562	—	68.85—68.95	844	—	”	90	0.67702	
6	68.95—69.1	1203	0.6825	68.95—69.03	1400	0.6803	”	110	0.67713	
7	69.1 — 69.2	1796	—	69.03—69.12	2040	—	”	122	0.67728	
8	69.2 — 69.35	1500	0.6856	69.12—69.20	2160	—	”	80	0.67755	
9	69.35—69.45	2317	—	69.2 — 69.3	1477	—	68.95—68.98°			
10	69.45—69.6	845	0.6933	69.3 — 69.4	1408	—				
11	69.6 — 69.8	421	—	69.4 — 69.5	1169	—				
12	69.8 — 70.15	227	0.7042	69.5 — 69.7	300	0.6962				
13	70.15—74.0	48	0.7306	69.7 — 69.95	330	0.7095				
14				69.95—70.15	310	0.7157				



It will be seen that the agreement is perfectly satisfactory. Lachowicz (*loc. cit.*) states that he separated normal hexane boiling at  $70^{\circ}$  from Galician petroleum. The presence of normal hexane in Russian petroleum has been recognised by Markownikoff and others.

*Methylpentamethylene.*

The rapid rise in specific gravity of the fractions between  $69^{\circ}$  and  $70.15^{\circ}$  (see previous table), together with the fact that the maximum value of  $\Delta w/\Delta t$  is at a temperature but slightly higher than  $69.0^{\circ}$ , indicates the presence of a hydrocarbon of high specific gravity, boiling but little higher than the paraffin.

The behaviour of the higher fractions, when treated with fuming nitric acid, shows that the heavy hydrocarbon is methylpentamethylene, which boils at about  $71.5^{\circ}$ , and has a sp. gr. of about 0.766 at  $0^{\circ}$ . Markownikoff (*Ber.*, 1897, 30, 1222) gives the constants for three specimens, prepared synthetically; Zelinsky (*Ber.*, 1897, 30, 389) gives those for a single specimen.

Observer.	Boiling point.	Sp. gr.
Markownikoff...	$71.5-72^{\circ}$ at 742 mm.	0.76829 at $0^{\circ}/0^{\circ}$
„ ...	$71-72$ „ 755 „	0.76641 „ „
„ ...	$70-72.5$ ?	0.76615 „ „
Zelinsky .....	$72^{\circ}$	0.7501 „ $21^{\circ}/4^{\circ}$

Both observers find that, whilst methylpentamethylene is not acted on by a mixture of nitric and sulphuric acids at the ordinary temperature and is but very slowly attacked at the boiling point of the hydrocarbon, great heat is evolved when it is shaken with fuming nitric acid, and Markownikoff states that the chief oxidation product, other than gases, is acetic acid.

As regards Russian petroleum, Markownikoff made a direct comparison of the fraction about  $70^{\circ}$  with synthesised methylpentamethylene, and showed that this fraction consisted of a mixture of normal hexane and methylpentamethylene. Aschan (*Ber.*, 1898, 31, 1803) also finds that the fractions about  $71^{\circ}$  behave like mixtures of methylpentamethylene with a paraffin. By heating the liquid with six times its volume of fuming nitric acid, he obtained large quantities of acetic and succinic acids, and a small quantity of an indifferent solid substance melting at  $185-187^{\circ}$ .\*

The fractions from  $69.95^{\circ}$  to  $70.15^{\circ}$  which I obtained from American petroleum became hot when shaken with fuming nitric acid, much

\* With ordinary concentrated nitric acid, Aschan found that nitrobenzene was formed in considerable quantity, but this was doubtless due to the presence of benzene, which would not, as he supposes, be removed by fractional distillation.

acetic acid being formed. The higher fractions generally, when heated with the fuming acid, were rapidly attacked at first, and after prolonged heating, considerable quantities of acetic acid and also oxalic and succinic acids were formed. In one case, a small amount (0.8 gram from 97 grams of hydrocarbon) of a solid nitro-compound melting at  $179-183^{\circ}$  was precipitated on diluting the acid; this was probably the same substance that Aschan obtained. In most other cases, small quantities of a liquid nitro-compound were formed.

Proceeding from the higher to the lower fractions, the action of fuming nitric acid became less and less marked and the loss of weight of hydrocarbon and production of nitro-compound diminished, until with the fraction  $68.95-69.03^{\circ}$  there was no development of heat on shaking with the acid, the loss of weight after heating for five days was only 20 per cent., a mere trace of liquid nitro-compound being formed. Below  $68.95^{\circ}$ , the loss of weight increased again, and crystals of the trinitro-derivative of isohexane were formed in larger and larger quantity.

The heavy hydrocarbon could not have been hexamethylene, which boils at  $80.8^{\circ}$ , does not become hot when shaken with fuming nitric acid, and, when heated with it, is oxidised chiefly to adipic acid.

### *Benzene.*

It was long ago stated by Schorlemmer (*Annalen*, 1863, 127, 311) that small quantities of aromatic hydrocarbons are present in American petroleum, but the apparently anomalous behaviour of mixtures of aromatic hydrocarbons with paraffins on distillation has given rise to some confusion. Some American "petroleum ether" was fractionated without previous treatment with mixed sulphuric and nitric acids, and the fractions between, say,  $60^{\circ}$  and  $80^{\circ}$  were then separately shaken with the mixed acids; it was found that the fraction from about  $65^{\circ}$  to  $66^{\circ}$  gave a large amount of metadinitrobenzene (m. p.,  $89.0-89.7^{\circ}$ ; mol. wt., 156—170; nitrogen, 16.98 and 16.84 per cent., calc., 16.67), whilst the fractions above and below these temperatures gave smaller and smaller quantities of the dinitro-compound. The fractions above about  $71^{\circ}$  and those below  $60^{\circ}$  gave, scarcely any dinitrobenzene.

Markownikoff, in his most recent paper (*Annalen*, 1898, 301, 169) states that he obtained very little dinitrobenzene from the fractions from  $50^{\circ}$  to  $60^{\circ}$ , a considerable amount from those from  $60^{\circ}$  to  $70^{\circ}$ , and the largest quantity from the fractions from  $70^{\circ}$  to  $80^{\circ}$ .

The formation of the largest amount of dinitrobenzene from the fraction from about  $65^{\circ}$  to  $66^{\circ}$  in the case of American petroleum was observed by Mr. G. L. Thomas and myself in 1895, and the most

probable explanation seemed to be that benzene and hexane, although miscible in all proportions, approximate in their behaviour to liquids that are only partially miscible, and a few rough experiments with mixtures of pure benzene and normal hexane confirmed this view. The subject has recently been carefully investigated by Dr. D. H. Jackson in this laboratory, and it appears that the boiling point of hexane is hardly affected by considerable additions of benzene, but that the boiling point of benzene is rapidly lowered by comparatively small additions of hexane. Also there is a marked expansion on mixing the hydrocarbons.

If, then, American petroleum contains a relatively small amount of benzene, it should come over for the most part at the boiling point of the hexane; but as both normal and iso-hexane are present in large quantity, the benzene should distil over mostly at somewhere about the mean boiling point of the two paraffins, that is, at about  $65^{\circ}$ .

In the fractionation of Russian petroleum, a larger amount of benzene comes over between  $70^{\circ}$  and  $80^{\circ}$  than between  $60^{\circ}$  to  $70^{\circ}$ , and if the two cases were strictly comparable, one might conclude with certainty that Russian petroleum is richer in benzene than American. Nothing, however, is known about the behaviour of mixtures of benzene with hexamethylene or with methylpentamethylene, and the great richness of Russian petroleum in these compounds makes it unsafe at present to draw a definite conclusion from the facts referred to.

Markownikoff, however, states that, in one case, he obtained 60 grams of dinitrobenzene from 1769 grams of petroleum boiling between  $60^{\circ}$  and  $84^{\circ}$ , that is, 3.4 grams per 100 of petroleum. I obtained 9.2 grams on one occasion from 417 grams of American petroleum boiling from  $57^{\circ}$  to  $77^{\circ}$ , or not quite 2 grams per 100 of petroleum. These results show that Markownikoff's sample of Russian petroleum was richer in benzene than my sample of American petroleum, but, obviously, a direct comparison carried out under similar conditions would be more satisfactory. Miss Fortey found that Galician petroleum was richer than American in benzene.

#### *Hexamethylene.*

In the fractionation of "petroleum ether" with the 12-column dephlegmator, carried out by Mr. Thomas and myself in 1895, it was noticed that between, say,  $57^{\circ}$  and  $88^{\circ}$ , in addition to the two maximum values of  $\Delta w/\Delta t$  at about  $61^{\circ}$  and  $69^{\circ}$ , there appeared to be a smaller one in the neighbourhood of  $80^{\circ}$ . The further examination of this portion of the petroleum was not continued until a year later, when it was found that a liquid of high specific gravity (0.754 at

0°/4°), boiling a little above 80° (79·95—80·35°) was actually present. The quantity, however, was insufficient for further purification, and Miss Fortey then undertook the fractional distillation of a much larger quantity of American "petroleum ether," with a view to the separation of this hydrocarbon, and she obtained it in a nearly pure state.

Meanwhile, the work of Markownikoff, Zelinsky, and others showed that a hexanaphthene, boiling near 80°, was present in large quantity in Russian petroleum. Markownikoff, in fact, obtained larger fractions from 80° to 82° than for the same range at any lower temperature. He showed (*Ber.*, 1897, 30, 974) that his hexanaphthene, on oxidation with fuming nitric acid, yielded adipic acid, and Miss Fortey found that her hexanaphthene from American petroleum gave the same acid. It has thus, and in other ways, been conclusively proved that the naphthene boiling at about 80° is really hexamethylene.

More recently, Miss Fortey has separated the same hydrocarbon in a pure state from Galician petroleum, and finds that its boiling point is 80·8°, and its sp. gr. is 0·79028 at 0°/4°.

*Isoheptane (and other Isomerides ?); Dimethylpentamethylene; Normal Heptane; Methylhexamethylene.*

The results obtained in the fractionation of the American petroleum boiling between, say, 88° and 105°, after removal of toluene, were very similar to those already described in the case of the hexanes. It was not possible to separate a hydrocarbon of constant boiling point, but there were maximum values of  $\Delta w/\Delta t$  at about 90·7° and 99·3°. Also, whilst the specific gravities of the fractions about the lower maximum showed but slight variation, those above 98° rose very rapidly indeed. The specific gravities were, however, in all cases, considerably higher than those of the pure paraffins.

The results of the ninth fractionation with the 12-column dephlegmator are given on p. 917.

After four more fractionations of the portion below 96°, the best fraction came over from 90·8—90·9°; the value of  $\Delta w/\Delta t$  had risen to 235, but the sp. gr. (0·71130) was practically unaltered. The boiling points and specific gravities (0°/4°) of the heptanes (normal heptane from *Pinus sabiniana*; isoheptane from ethylic and amylic bromides with sodium) have been determined by Thorpe (*Trans.*, 1880, 37, 73 and 76) as below.

	Boiling point.	Specific gravity.
Isoheptane .....	90·3°	0·69692
Normal heptane .....	98·43	0·70048

No. of fraction.	Temperature.	$\frac{\Delta w}{\Delta t}$ .	Specific gravity 0°/4°.
1	86.5 — 89.1°	8.0	0.72767
2	89.1 — 90.25	28.4	—
3	90.25 — 90.55	100.4	0.71136
4	90.55 — 90.7	183.3	0.71123
5	90.7 — 91.0	145.3	—
6	91.0 — 91.6	76.2	0.71273
7	91.6 — 93.0	22.2	—
8	93.0 — 96.3	8.2	—
9	96.3 — 98.0	12.1	—
10	98.0 — 98.65	37.7	0.71521
11	98.65 — 99.1	67.3	0.71991
12	99.1 — 99.35	116.4	0.72630
13	99.35 — 99.65	113.7	0.73374
14	99.65 — 100.25	53.2	0.74476
15	100.25 — 101.1	36.5	0.75572
16	101.1 — 103.8	7.6	0.75667

It will thus be seen that the specific gravity of the isoheptane partially separated from the petroleum is considerably higher than that of the synthesised product. This may possibly be due to the difficulty of separating hexamethylene and methylhexamethylene, which are present in considerable quantity; or it may be due to the presence of a small quantity of dimethylpentamethylene which is stated by Zelinsky (*Ber.*, 1897, 30, 1532) to boil at about 94° and to have the sp. gr. 0.7543 at 20°/4°, and is believed by Markownikoff (*Annalen*, 1898, 301, 170) to be present in Russian petroleum in large quantity in the fraction 90—92°.

As regards normal heptane, the maximum value of  $\Delta w/\Delta t$  is at about 99.4° instead of 98.4°, and this fact, together with the very rapid rise of specific gravity from 98° to 101°, indicates the presence of a heavy hydrocarbon in considerable quantity, with a boiling point a very few degrees higher than that of normal heptane.

There can be little doubt that this hydrocarbon is methylhexamethylene, which both Markownikoff and Zelinsky find in Russian petroleum.

Zelinsky (*loc. cit.*) gives the boiling point of this naphthene as 101° and its sp. gr. as 0.7694 at 20°/4°.

From some preliminary experiments on a small scale with fractions 11—13, it seemed probable that, by bromination of the hydrocarbon, fractionation to separate monoheptylic bromide, and reduction of the bromide, pure normal heptane might be obtained from the petroleum. A large quantity of mixed heptanes from American petroleum has been treated in this way by Dr. F. E. Francis, with the result that isoheptane has been obtained in a fairly pure state (b. p. 89.9—90.4°;



sp. gr. 0.70670 at  $0^{\circ}/4^{\circ}$ ), and normal heptane very nearly pure (b. p.  $98.25-98.45^{\circ}$ ; sp. gr. 0.70186 at  $0^{\circ}/4^{\circ}$ ).

The boiling points agree well in both cases with those observed by Thorpe. The specific gravity of the normal heptane is slightly, and of the isoheptane considerably, too high, but the quantity of material, especially in the latter case, was too small to admit of complete purification. The results are fully described in a separate paper.

Up to the present time, little, if any, evidence has been obtained of the presence of other isomeric heptanes in American, Galician or Russian petroleum, unless, possibly, the difficulty experienced in separating hexamethylene in a quite pure state from American petroleum may point to the presence in very small quantity of a heptane boiling at a temperature not far from  $80^{\circ}$ .

### *Toluene.*

Toluene is present in considerable quantity in American petroleum and, like benzene, it comes over chiefly at a temperature far below its ordinary boiling point.

It is easily removed by repeated agitation with a mixture of nitric and sulphuric acids; by diluting the acid, several nitro-compounds are precipitated, chiefly the dinitrotoluene melting at  $72.5^{\circ}$ .

Markownikoff also finds that homologues of benzene are present in large quantity in Russian petroleum.

The results which have been described show that the same classes of hydrocarbons, paraffins, polymethylene compounds or naphthenes, and aromatic hydrocarbons are present in petroleum from all three sources, but that Russian petroleum contains a relatively larger amount of naphthenes, and, in all probability, of aromatic hydrocarbons than Galician, and Galician a larger amount of the same hydrocarbons than American petroleum.

In conclusion, it may be well to point out some striking points of agreement in the results obtained in the fractionation of Russian and American petroleum.

Markownikoff gives details of the fractionation of two samples of Russian petroleum from which aromatic hydrocarbons had been previously removed. The range of temperature for each fraction was  $2^{\circ}$ , so that the weights of the fractions are proportional to the ratios  $\Delta w/\Delta t$ , and a direct comparison can therefore be made with the results described in this paper.

Data for both samples of Russian petroleum for the fractions from  $58-76^{\circ}$  and from  $86-106^{\circ}$  are given below, and may be compared with the tables in this paper for isohexane, normal hexane, and iso- and normal heptanes (pp. 909, 911, §917).

Boiling point.	I.		II.	
	Weight in grams.	Sp. gr. 15°/15°.	Weight in grams.	Sp. gr. 15°/15°.
58— 60°	115	0·667	144	0·668
60— 62	262	0·667	278	0·666
62— 64	139	0·668	698	0·668
64— 66	166	0·675	408	0·673
66— 68	107	0·683	346	0·680
68— 70	330	0·698	547	0·692
70— 72	638	0·723	971	0·712
72— 74	514	0·739	1375	0·731
74— 76	262	0·745	831	0·745
86— 88	336	0·739	281	0·735
88— 90	308	0·736	474	0·729
90— 92	1682	0·731	1239	0·726
92— 94	676	0·729	387	0·730
94— 96	133	0·740	298	0·738
96— 98	114	0·746	148	0·741
98—100	26	0·752	255	0·753
100—102	—	—	1041	0·758
102—104	—	—	934	0·758
104—106	—	—	556	0·753

The following points of agreement between my results and Markownikoff's may be noticed.

1. The specific gravities of the fractions boiling at from 58—64° show but slight variation, and are but little, if at all, higher than that of isohexane (this is not yet known with accuracy, but must be somewhat lower than that of normal hexane).

2. The specific gravities of the fractions from 68—74° rise very rapidly and are considerably higher than that of normal hexane.

3. The maximum value of  $\Delta w/\Delta t$  at about 72° (Markownikoff), 69° (Young), is very much higher than that at about 62° (61°, Young).

4. The specific gravities of the fractions from 86—94° do not vary much, but show a minimum at about 92° (Markownikoff), 91° (Young). They are, however, considerably higher than that of isoheptane.

5. The specific gravities of the fractions from 96—102° (98—101°, Young) rise much more rapidly, reaching a maximum at about 102°. They are much higher than that of normal heptane.

6. The maximum value of  $\Delta w/\Delta t$  is rather greater at about 91° than at about 101° (99·5 Young).

On the other hand, Markownikoff's fractions from 80—82° were exceedingly large [weights, 1582 and 1940 grams; sp. gr. 15°/15°, 0·760 and 0·755], showing the great richness of Russian petroleum in naphthenes. With American petroleum, this fraction would be very

much smaller than those about the boiling points of the hexanes and heptanes.

It may finally be mentioned that Markownikoff has examined a number of samples of Russian petroleum from different sources, and finds considerable variation in the relative amounts of paraffin naphthenes present in them.

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## XCII.—*Separation of Normal and Iso-heptane from American Petroleum.*

By FRANCIS E. FRANCIS, B.Sc., Ph.D., and SYDNEY YOUNG, D.Sc.,  
F.R.S.

AN attempt made by one of us to separate the heptanes from American petroleum by fractional distillation, after removal of toluene by treatment with a mixture of nitric and sulphuric acids, was unsuccessful, owing to the presence of polymethylene compounds in the petroleum.

It seemed possible, however that, by the action of bromine, the polymethylene compounds might yield higher bromine derivatives more readily than the paraffins, and that the heptylic monobromides might thus be obtained in a pure state. The bromides could then be reduced to the corresponding paraffins by means of nascent hydrogen.

A preliminary experiment with about 90 grams of the fractionated petroleum, boiling between  $98.65^{\circ}$  and  $99.65^{\circ}$  and containing chiefly normal heptane and methylhexamethylene, gave promising results, a small quantity of a bromide boiling at about  $93^{\circ}$  under a pressure of 70 mm. being obtained.

It was then decided to brominate a large quantity of the mixed heptanes—containing a considerable amount of methylhexamethylene, a little hexamethylene, and possibly some dimethylpentamethylene.

In the first experiment, 900 grams of bromine were gradually added to 760 grams of the petroleum (b. p.  $96.5-102^{\circ}$ ), small quantities of aluminium bromide being introduced from time to time. In this case, however, higher bromides of both the paraffins and polymethylene compounds were chiefly formed, for, on distillation, 605 grams of unaltered petroleum were recovered, and no monobromides could be isolated from the residue.

The second bromination was carried out without the use of aluminium bromide, and the temperature was raised only just sufficiently for the action to take place. In this case, 517 grams of hydrocarbon (b. p. 95—101°), and 850 grams of bromine yielded 730 grams of bromides and 180 grams of unaltered petroleum. By repeated fractionation under reduced pressure (70 mm.), 87·5 grams of monobromide, boiling at 93—94·5° were obtained. The bromide was then reduced in alcoholic solution with a zinc-copper couple, small quantities of saturated hydrochloric acid being added from time to time. The paraffin, separated with water, washed, dried, and distilled, gave 48·3 grams of heptane and 17·5 grams of unaltered bromide. The heptane boiled mostly at 98°, and its sp. gr. was 0·70393 at 0°/4°. After treatment with a mixture of sulphuric and nitric acids, this was reduced to 0·70238.

A third quantity of petroleum (760 grams), richer in isoheptane (b. p. 93·5—102°), was then brominated at a higher temperature, the unaltered hydrocarbon being distilled off from time to time, and again heated with bromine. The bromides were then distilled under reduced pressure and the monobromides were fractionated fourteen times with the 12 column dephlegmator under a pressure of 70 mm.

*Normal heptylic bromide* was obtained with constant boiling point, 93·0°, under 70 mm. pressure. Its sp. gr. at 0 /4° was 1·1577.

*Isoheptylic bromide* was separated in a fairly pure state; b. p. 82—84·2°, mostly at 83—84°, under a pressure of 70 mm. When distilled from a bulb with short still-head, most of it came over at 84°. The sp. gr. was 1·1667 at 0°/4°.

The normal heptylic bromide was reduced in the same manner as before, and the normal heptane, after one distillation, boiled at 98·35—98·5°; the sp. gr. was 0·70314.

The whole of the normal heptane was then heated with fuming nitric acid, washed with caustic soda, then with water, dried over phosphorus pentoxide, and distilled with the 12-column dephlegmator. The boiling point was now 98·2—98·5° and the sp. gr. 0·70186.

It is probable that the heptane still contained a very small quantity of nitro-compound, which would raise its specific gravity, but it was evidently very nearly pure. The critical consonants were then determined with the portion coming over between 98·25° and 98·45°, also the vapour pressures and specific volumes at a few temperatures. The results are given in the table below, together with the corresponding constants determined with Dr. Thorpe's well known specimen of normal heptane from *Pinus sabiniana*. In the calculation of the volumes of a gram, the sp. gr. at 0° was taken to be 0·70048, and not 0·70168.

	Normal heptane from	
	Petroleum.	<i>Pinus sabiniana</i> .
Boiling point.....	98·25—98·45°	98·43°
Specific gravity 0°/4° .....	0·70186	0·70048
Critical temperature.....	267·0°	266·85°
„ pressure .....	20550 mm.	20430 mm.
„ volume of a gram .....	4·261 c.c.	4·266 c.c.
Vapour pressure at 130° .....	1773	1753
„ „ 240 .....	13825	13790
„ „ 260 .....	18530	18470
Volume of a gram of liquid at 130° .....	1·717 c.c.	1·7176 c.c.
„ „ „ 240 .....	2·390	2·394
„ „ „ 260 .....	2·882	2·895
Volume of a gram of saturated vapour at 240° ...	13·45 c.c.	13·43
„ „ „ 260 ...	7·796	7·77

It will be seen that the critical temperatures and the volumes of a gram agree very well indeed, but the pressures show somewhat greater differences.

The isoheptylic bromide was similarly reduced, and the paraffin was treated for a short time with fuming nitric acid, but it was rapidly attacked and the quantity was so seriously diminished that no fractionation was possible, and it could only be once distilled.

The boiling point was 89·9—90·4° and the sp. gr. 0·70670 at 0°/4°.

Thorpe determined the boiling point and specific gravity of a specimen prepared by the action of sodium on a mixture of ethylic and amylic bromides and obtained the values 90·3° and 0·69692 at 0°/4°.

There can be little doubt that the isoheptane from petroleum contained some nitro-compound, which would raise the specific gravity. From its boiling point, it would appear to be identical with Thorpe's specimen.

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### XCIH.—*Specific Gravities and Boiling Points of Mixtures of Benzene and Normal Hexane.*

By D. HAMILTON JACKSON, M.A., B.Sc., Ph.D., and SYDNEY YOUNG, D.Sc., F.R.S.

IN the fractional distillation of "petroleum ether" from which the aromatic hydrocarbons had not been previously removed by treatment with a mixture of nitric and sulphuric acids, it was observed that the



benzene and toluene, unlike the polymethylene hydrocarbons, did not come over at their true boiling points, but chiefly about  $15^{\circ}$  lower. Thus the portion richest in benzene \* was that boiling at about  $65^{\circ}$ , the amount of benzene diminishing regularly at higher and lower temperatures. This lowering of the boiling point of benzene, when mixed with hexanes, seemed to indicate that paraffins and aromatic hydrocarbons, although miscible in all proportions, behave as regards distillation in a manner comparable with that of liquids only partially miscible. A few rough experiments on the distillation of mixtures of benzene and normal hexane in different proportions appeared to support this view, and it was thought desirable to make a more complete investigation of the boiling points and specific gravities of mixtures of these hydrocarbons.

Both the normal hexane and the benzene employed were obtained from Kahlbaum. The *hexane* was purified before use, according to the method given in a preceding paper (Trans., 1895, 67, 1071), and then dried with phosphorus pentoxide and with sodium; it boiled at  $68.97^{\circ}$  (corr.); its sp. gr.  $0^{\circ}/4^{\circ}$  was 0.67705. The *benzene* was shaken up with small quantities of strong sulphuric acid, washed with water, and dried with phosphorus pentoxide and with sodium; it boiled at  $80.21^{\circ}$  (corr.); its sp. gr.  $0^{\circ}/4^{\circ}$  was 0.90005.

*Determination of the Specific Gravities of Mixtures of Benzene and Normal Hexane.*—The method employed was as follows. The benzene was poured from a U-tube drawn out to a capillary at either end, into a small very short-necked mixing flask, the weight of which was known, and the added weight was determined. The hexane was then introduced, and its weight similarly determined. From these data, the composition of the mixture was deduced.

After shaking, the mixed liquids were sucked up into a Sprengel specific gravity tube (Perkin's form) of the capacity 15.325 c.c. at  $0^{\circ}$ , and the specific gravity was ascertained in the ordinary way. Although the total loss of benzene *plus* hexane in pouring out these liquids from the U-tubes in which they were contained into the mixing flask was not inconsiderable, it was found that the loss during the manipulation of the prepared mixture was such as not sensibly to affect the values of the specific gravity obtained. This was shown by making redeterminations of the specific gravity with the same liquid as follows. Rather more of a mixture was prepared in the mixing flask than was necessary for a single estimation of the specific

\* The presence of benzene in such a mixture of hydrocarbons is readily detected, and its amount approximately ascertained, by prolonged treatment—several times repeated if it is desired to remove the benzene completely—with a mixture of concentrated nitric and sulphuric acids. On diluting the acid with water, and allowing it to stand for two or three days, metadinitrobenzene crystallises out.

gravity, and a determination was then made; immediately after, the liquid used was blown back from the Sprengel tube into the mixing-flask and a second determination made; this second value for the specific gravity was not usually greater than the first by 0.01 per cent. The results of the specific gravity determinations are given in the following table.

Mixture.	Percentage of benzene.	Observed sp. gr. 0°/4°.	Observed vol. of a gram $= \frac{1}{\text{sp. gr.}}$	Calculated* vol. of a gram.	Increase of vol. of a gram on mixing.
I.	1.24	0.67896	1.47284	1.47244	0.00040
II.	1.52	0.67952	1.47163	1.47143	0.00020
III.	9.27	0.69212	1.44483	1.44306	0.00177
IV.	12.31	0.69723	1.43425	1.43195	0.00230
V.	15.07	0.70196	1.42458	1.42184	0.00274
VI.	16.95	0.70535	1.41773	1.41497	0.00276
VII.	21.57	0.71342	1.40169	1.39807	0.00362
VIII.	22.41	0.71501	1.39857	1.39499	0.00358
IX.	24.22	0.71821	1.39235	1.38837	0.00398
X.	31.87	0.73258	1.36504	1.36036	0.00468
XI.	33.23	0.73517	1.36023	1.35538	0.00485
XII.	36.51	0.74166	1.34832	1.34338	0.00494
XIII.	38.38	0.74528	1.34178	1.33654	0.00524
XIV.	40.40	0.74936	1.33448	1.32914	0.00534
XV.	41.39	0.75153	1.33061	1.32552	0.00509
XVI.	41.54	0.75184	1.33007	1.32496	0.00511
XVII.	47.03	0.76326	1.31016	1.30489	0.00527
XVIII.	55.30	0.78140	1.27975	1.27463	0.00512
XIX.	63.58	0.80057	1.24910	1.24432	0.00478
XX.	69.18	0.81394	1.22858	1.22385	0.00473
XXI.	70.78	0.81797	1.22253	1.21796	0.00457
XXII.	77.38	0.83492	1.19772	1.19382	0.00390
XXIII.	79.85	0.84142	1.18846	1.18477	0.00369
XXIV.	81.34	0.84548	1.18276	1.17933	0.00343
XXV.	86.27	0.85916	1.16393	1.16129	0.00264
XXVI.	88.61	0.86586	1.15492	1.15273	0.00219
XXVII.	91.58	0.87436	1.14369	1.14184	0.00185
XXVIII.	92.80	0.87802	1.13892	1.13739	0.00153
XXIX.	95.20	0.88514	1.12975	1.12861	0.00114

\* That is, on the assumption that there is no change of volume on mixing the benzene and hexane. Let  $p$  = percentage of benzene; then, taking 0.90005 as the sp. gr. of benzene, and 0.67705 as that of hexane, we have

$$\frac{p}{100 \times 0.90005} + \frac{100-p}{100 \times 0.67705} = \text{calculated vol. of a gram.}$$

*Determination of the Boiling Points of Mixtures of Benzene and Normal Hexane.*—For this purpose, Beckmann's boiling point apparatus was used, and the method finally employed was practically the same as that of Nernst in his investigation of the boiling points of benzene and acetic acid (*Zeit. physik. Chem.*, 1891, 8, 110). An upright glass tube, however, was used in place of the usual glass spiral condenser

attached to the inner boiling tube. As the range of temperature between the boiling points of benzene and hexane is considerable, it was decided to substitute for the ordinary Beckmann, an open-scale Geissler thermometer divided into half degrees and easily allowing readings to be made to  $0.05^{\circ}$ .

The benzene and hexane were placed in U-tubes provided with wide capillaries, and the amount of liquid used in an experiment was ascertained by weighing the tubes before and after pouring. One of the liquids was introduced in the cold; the other was added by pouring it down the straight condenser tube as soon as the first had been brought to steady ebullition. Benzene was the liquid used throughout in the outer jacket of the apparatus.

The height of liquid in the boiling tube in the case of the mixture is, of course, not the same as that of the single liquid (benzene or hexane), so that the observed boiling points are not strictly comparable. It was found, however, experimentally (by observing the boiling point of benzene in the apparatus and then adding further successive quantities of benzene and observing the boiling point) that the error from this cause was negligible, being less than the limit to which the thermometer was read.

To ascertain the error due to change of composition of the mixture during an experiment, the composition of the liquid also *after* the experiment was ascertained by utilising the specific gravity results given above. The latter were plotted out on an open scale against the percentage composition, so that the strength corresponding with a specific gravity could be read off. After a determination of strength and boiling point had been made in the ordinary way, the apparatus was allowed to cool down, the mixture from the inner tube was poured into a small flask, and from the latter it was sucked up into the specific gravity tube. It was found that the strength of the mixture as determined by the two methods was the same to within less than 0.2 per cent., as a rule. Now, if the boiling points given in the table below be examined, it will be seen that an error of 0.2 per cent. in the estimation of the strength is negligible with a thermometer read to twentieths of a degree, except in the case of mixtures containing 90–100 per cent. of benzene where a small change in composition produces a relatively large change in boiling point. In the case of these mixtures, it is probable that the error in the boiling point exceeds one-twentieth of a degree, if the strengths are taken as correct; the indirect method of ascertaining the percentage composition would no doubt be preferable in this case, but its application is difficult owing to the readiness with which mixtures very rich in benzene freeze in the specific gravity tube when cooled to  $0^{\circ}$ .

The following are the results of the boiling point determinations

the strengths given being those obtained by weighing, and not by the specific gravity method. Probably the true strengths would lie between those obtained by the two methods.

Mixture.	Percentage of benzene.	Boiling point (corr.).*	Mixture.	Percentage of benzene.	Boiling point (corr.).*
I.	5.5	69.00°	XI.	64.9	72.70°
II.	6.5	68.96	XII.	67.3	73.01
III.	11.6	69.00	XIII.	78.0	74.67
IV.	17.2	69.14	XIV.	78.8	74.75
V.	27.3	69.47	XV.	85.2	76.12
VI.	31.6	69.72	XVI.	88.9	76.91
VII.	39.5	70.17	XVII.	90.1	77.20
VIII.	46.6	70.70	XVIII.	92.0	77.75
IX.	47.3	70.70	XIX.	94.0	78.49
X.	53.0	71.42	XX.	95.3	78.80

\*  $dp/dt$  at 760 mm. = 23.3 mm. for benzene. For hexane, the value is 23.9 mm.; it was given by mistake as 22 mm. in the original paper (Trans., 1895, 67, 1072). The boiling point of hexane at 760 mm. should be 68.95°, and not 69.0° as previously (*loc. cit.*) stated.

It is well known that the members of many homologous series of organic compounds become less and less soluble in water as the molecular weight increases; this is notably the case with the saturated fatty alcohols,  $C_nH_{2n+2}O$ , and acids,  $C_nH_{2n}O_2$ , the lowest members of which, methylic alcohol and formic acid, are miscible with water in all proportions, whilst the very high members are practically insoluble at ordinary temperatures. At the same time, experimental evidence, so far as it goes, points to the conclusion that the contraction and heat evolution diminish with rise of molecular weight. Konowaloff, in his study of the vapour pressures of mixtures of the lower alcohols with water (*Ann. Chem. Phys.*, 1881, [ii], 14, 34), has shown that there is here also a gradual change from the ordinary behaviour of two miscible liquids (methylic alcohol and water), the vapour pressures of which, and also the boiling points, are always intermediate between those of the components, to that of partially miscible liquids, mixtures of which, within certain limits, have vapour pressures higher, and boiling points lower, than that of either component; a somewhat similar result was obtained by the study of the vapour pressure of mixtures of the fatty acids with water.

Konowaloff observed, however, that, starting from the lowest member of a series, the typical form of curve for partially miscible liquids was reached, both with the alcohols and acids, before the liquids ceased to be miscible in all proportions at ordinary temperatures.

Thus methylic, ethylic, and propylic alcohols are each of them



miscible with water in all proportions, but whilst the vapour pressure of methylic alcohol diminishes regularly on dilution, that of ethylic alcohol is hardly affected by the addition of a moderate amount of water; it shows, indeed, a very slight rise at first, but afterwards diminishes at an increasing rate, until, with infinite dilution, the vapour pressure of pure water is reached.

With propylic alcohol and water, there is, at each temperature, a certain mixture which has a very decided maximum vapour pressure considerably higher than that of either component. Conversely, there is at each pressure a particular mixture of propylic alcohol and water which, like a pure liquid, distils at a constant temperature and with constant composition. On distilling stronger or weaker solutions of propylic alcohol and water, the mixture of maximum vapour pressure and minimum boiling point comes over first, followed by mixtures richer in propylic alcohol or water, according to the original composition. It is, therefore, possible to separate either pure propylic alcohol or pure water, but not both, from such a mixture.

With ethylic alcohol and water, since the maximum vapour pressure (and minimum boiling point) differs but very slightly from that of pure alcohol and corresponds with a mixture containing very little water, it follows that a very strong solution of ethylic alcohol must distil over at a nearly constant temperature and almost without change of composition, and that neither pure alcohol nor pure water can be separated from it. On the other hand, it is quite easy to obtain pure water by the distillation of a weak solution of ethylic alcohol.

As the boiling point of methylic alcohol rises steadily on dilution, both components may be separated by distillation of a mixture of the two.

Mixtures of water with acetic acid behave like those of ethylic alcohol and water, except that no maximum vapour pressure has been observed. The vapour pressure of water is but slightly lowered by adding a little acetic acid, whilst that of acetic acid is rapidly raised by the addition of water; and it is quite possible to obtain anhydrous acetic acid by the distillation of a strong aqueous solution, although it is very difficult, if not impossible, to separate either pure water or pure acetic acid by distillation of a weak solution of the acid.

The data given above show that mixtures of normal hexane and benzene behave, on distillation, in a similar manner to mixtures of ethylic alcohol and water or of water and acetic acid. An addition of 10 per cent. of benzene to normal hexane has no appreciable influence on the boiling point, whilst an addition of 10 per cent. of hexane to benzene lowers the boiling point nearly  $3^{\circ}$ . Again, from a solution containing, say, 10 per cent. of benzene, it is impossible to separate either component by fractional distillation, but it would be



easy to separate pure benzene, but not hexane, from a mixture containing, say, 90 per cent. of benzene.

That the liquids do approximate in their behaviour to partially miscible liquids is further shown by the fact that there is always expansion on mixing, the expansion reaching a maximum of about 0.4 per cent.

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#### XCIV.—*Action of Fuming Nitric Acid on the Paraffins and other Hydrocarbons.*

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F.R.S.

It is usually stated that nitric acid—concentrated, fuming, or mixed with sulphuric acid—has little or no action on the paraffins, whilst in one or other form it acts readily on the unsaturated and aromatic hydrocarbons, yielding nitro-compounds in the latter case. It has, however, been observed by Konowaloff (*Ber.*, 1892, 25, Ref. 108) that normal hexane and octane yield secondary nitro-compounds when heated with dilute nitric acid in sealed tubes at 130–140°.

Hydrocarbons of the polymethylene series are not attacked by a mixture of sulphuric and nitric acids at the ordinary temperature, nor readily on moderate heating. With fuming nitric acid, the behaviour of pentamethylene and hexamethylene differs widely from that of their methyl derivatives, for the two former compounds are only attacked when heated, and yield chiefly the corresponding dibasic acids—glutaric and adipic acids—whilst the methyl derivatives, and especially methylpentamethylene, are acted on rapidly at the ordinary temperature with evolution of heat, and the molecule is for the most part broken down.

With less concentrated nitric acid at a high temperature, pentamethylene and hexamethylene give secondary nitro-compounds in addition to the dibasic acids, and the methyl derivatives yield tertiary nitro-compounds (Markownikoff, *Ber.*, 1897, 30, 974 and 1222; *Annalen*, 1898, 301, 201; Zelinsky, *Ber.*, 1897, 30, 389).

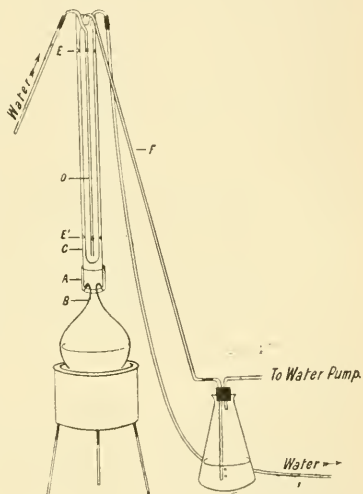
It is quite true that at the ordinary temperature the paraffins remain practically unacted on by nitric acid in any form, and that the normal paraffins are very slowly decomposed by fuming nitric acid when heated on a water bath, but we have observed that the iso-paraffins—iso-hexane, iso-heptane, iso-octane, di-isobutyl—are very readily attacked when heated with the fuming acid, a moderate yield of nitro-compound being obtained in each case.

*Isohexane.*

The attempt to separate normal hexane from light petroleum by fractional distillation, after removal of benzene, was only partially successful, owing to the presence of methylpentamethylene, which boils only about  $3^{\circ}$  higher than the paraffin. In order to remove the naphthene, the fractions from about  $66\text{--}70^{\circ}$  were separately heated with fuming nitric acid in a flask of special form provided with a reflux condenser (see Fig. 1). A

piece of wide tubing, A, is sealed to the narrow neck, B, of the round-bottomed flask, and the wide tube is pushed down over the narrow one so as to form a ring-shaped depression in which the tube C fits loosely. The condenser, D, is an internal one, somewhat like that recommended by Sudborough and Feilmann (*J. Soc. Chem. Ind.*, 1897, 16, 979), and is centred by five internal projections in the wide vertical tube in each of two horizontal planes E, E'. A little strong nitric acid in the ring-shaped depression prevents the escape of nitrous fumes below, and the gases which reach the top of the tube are carried off through a bent tube, F, connected with a wash bottle and a water pump. It is not

FIG. 1.



necessary to carry on the operation in a draught chamber.

Taking the fractions in descending order of temperature, it was observed that the loss of weight reached a minimum at about  $69^{\circ}$ , just above the true boiling point of normal hexane, increasing rapidly at lower temperatures. Also, whilst the higher fractions, rich in methylpentamethylene, gave diminishing amounts of a liquid nitro-compound (separated by diluting the acid with water) the fraction from  $68.85\text{--}68.95^{\circ}$  yielded no nitro-compound at all, and the lower ones, containing isohexane, gave increasing quantities of a solid nitro-compound.

Details of the results obtained with the fractions below  $69.03^{\circ}$ , including one from  $62.6\text{--}63.05^{\circ}$ , very rich in isohexane, are given in the table below. Each fraction was heated for 5 days with about its own volume of fuming nitric acid (renewed on the second and

fourth days), but in the case of the lowest fraction the treatment was extended to 6 days, and a fourth quantity of acid was used.

Temperature range.	Weight of fraction.		Percent- age loss.	Remarks.
	Before.	After.		
68.95—69.03	113.2	89.8	20.7	Trace of liquid nitro-compound.
68.85—68.95	84.4	66.1	21.7	Acid nearly clear on dilution.
68.7 —68.85	73.5	57.1	22.3	A few small crystals on standing.
68.35—68.7	83.0	60.8	26.7	0.6 gram solid nitro-compound.
67.85—68.35	51.0	32.0	37.3	1.1 " " " "
66.4 —67.85	79.4	37.4	52.9	4.9 " " " "
62.6 —63.05	89.2	6.5	92.7	12.0 " " " " also some liquid, b. p. about 194°.

The diluted nitric acid from the lowest fraction was found to contain a considerable quantity of acetic acid, some propionic acid, and very small quantities of oxalic and succinic acids.

The hydrocarbon remaining after treatment with nitric acid was in each case shaken repeatedly with strong sulphuric acid, until the latter gave no turbidity on dilution, then with caustic soda, and finally with water; after this, it was dried with phosphorus pentoxide and weighed.

Each fraction was distilled over sodium wire and it was found that, after a few fractionations (omitting the lowest fraction) to remove the last traces of nitro-compounds, the boiling point was quite constant at 68.95°, and the sp. gr. at 0°/4° rose only from 0.67693—0.67713, whereas, before treatment, the range of temperature was from 66.4 to 69.03° and of sp. gr. from 0.6793 to 0.6803. The remaining hydrocarbon therefore consisted of practically pure normal hexane (b. p. 68.95°; sp. gr. 0.67697) and both the pentamethylene, which raised the specific gravity, and the isohexane, which lowered the boiling point, had been eliminated.

The solid nitro-compound crystallised from light petroleum in hexagonal plates; recrystallised from petroleum or from alcohol, the melting point was 85.5—86.0°. Heated in an open tube with a free flame, it decomposed with slight explosion. The substance was analysed, with the following results.

	Found.		Calculated for $C_6H_{11}(NO_2)_3$ .
	I.	II.	
C .....	32.85	32.15	32.57 per cent.
H .....	5.37	5.26	4.97 " "
N .....	19.45		19.00 " "

It was therefore a trinitro-derivative of isohexane, and was probably a tertiary compound, as it appeared to give no reaction with nitrous acid and no sodium salt.

### *Isoheptane.*

A specimen of nearly pure isoheptane, prepared from the crude heptanes from petroleum by bromination, separation of the monobromides, and reduction of the isoheptylic bromide, was heated for a short time with fuming nitric acid, when it diminished quickly in volume, and the acid, on dilution, gave a considerable amount of a liquid nitro-compound.

A further quantity of less pure isoheptane, mixed with its own volume of normal hexane to dilute it, was heated with fuming nitric acid on the water bath for 2 days. As the acid, on dilution, again gave a liquid nitro-compound, it was distilled with steam until the oil had almost ceased to come over; the residue, on cooling, deposited crystals in small quantity. The solid nitro-compound, crystallised from a mixture of alcohol, water, and ether, melted at  $194^{\circ}$  with immediate decomposition. On recrystallisation, it was obtained in well-formed plates which melted at the same temperature.

The percentage of nitrogen was found to be 17.64. Calculated for  $C_7H_{13}(NO_2)_3 = 17.87$ .

### *Iso-octane.*

A specimen of iso-octane from petroleum, treated in the same manner as isoheptane, was quickly acted on, and gave a liquid nitro-compound, but in this case no solid could be separated by distillation with steam.

### *Isopentane.*

The boiling point of pure isopentane is too low for any reaction to take place with fuming nitric acid. It was thought possible, however, that a mixture of isopentane and normal hexane might give a high enough temperature, but the action was slow and the acid, on dilution, remained quite clear. The remaining hydrocarbon, when distilled, left a very small, semi-solid residue which, after being dried on a porous plate and recrystallised from dilute alcohol, melted at  $192^{\circ}$  with immediate decomposition. The quantity was too small for a nitrogen determination, but on heating it in a dry test tube, large quantities of red fumes were evolved. It thus resembled the trinitro-derivative of isoheptane very closely indeed.

*Di-isobutyl.*

A small quantity of di-isobutyl (from isobutylic bromide and sodium) mixed with its own volume of normal hexane, was heated for two days with fuming nitric acid on the water bath.

The acid, when diluted, became but slightly turbid, but the remaining paraffin, after being washed with dilute caustic soda, deposited crystals.

By recrystallisation from benzene and light petroleum, the nitro-compound was obtained in large, colourless plates melting at  $91.0^{\circ}$ .

The percentage of nitrogen was found to be 16.65. Calculated for  $C_8H_{15}(NO_2)_3 = 16.86$ .

*General Conclusions.*

The normal paraffins are less easily attacked by fuming nitric acid than any other hydrocarbons, and next to them come the polymethylene compounds with no side chains. Of the remaining hydrocarbons, the aromatic compounds, the methyl derivatives of the polymethylene hydrocarbons, and the iso-paraffins—which are all characterised by the presence of  $\equiv CH$  groups—are much more readily attacked, the first two classes of hydrocarbons at the ordinary temperature, the iso-paraffins when heated moderately on a water bath. Compounds of the general formula,  $(CH_3)_3C \cdot C_nH_{2n+1}$ , have not yet been studied, but, as they contain no  $\equiv CH$  group, it seems probable that they would resemble the normal paraffins in their behaviour with nitric acid.

A recent observation by Aschan (*Ber.*, 1898, 31, 1801) is of considerable interest in connection with this subject. Aschan finds that di-isopropyl and isopentane are rapidly attacked by chlorosulphonic acid at the ordinary temperature; he has not yet, however, studied the action of this reagent on other paraffins, but expresses the intention of doing so. It will be interesting to know whether the normal paraffins are less easily attacked than the iso-compounds.

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BRISTOL.

## XCV.—*Hexamethylene from American and Galician Petroleum.*

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THE object of the present research, undertaken at the suggestion of Professor Sydney Young, was, by means of fractional distillation, to obtain hexamethylene in a pure state from petroleum, with a view to the



accurate determination of its physical properties, and to prepare some of its derivatives, amplifying the work of Markownikoff (*Ber.*, 1895, 28, 577; 1897, 30, 1225) and at the same time repeating a portion of that of Baeyer (*Ber.*, 1893, 26, 229; *Annalen*, 1893, 278, 88) on the synthetical hydrocarbon. The presence of hexamethylene had been detected in American petroleum by Professor Young while engaged in the isolation of some of the paraffins, and that source was the one first employed, on account of the difficulty in procuring the Caucasian oil. The distillation was carried out with the aid of a fractionating column kindly made for the purpose by Professor Young, and similar to that described by him in the *Chemical News* (1895, 71, 177), but containing twelve constrictions instead of seven. The fractional distillation occupied about six months, at the expiration of which time it became evident that it would not be possible to obtain the hydrocarbon in a pure state, although the fractions obtained would serve for the preparation of its derivatives. The purest fraction boiled at 80.55–80.65°, sp. gr. 0.7722 at 0°/4°. A supply of Galician petroleum was next procured, and the distillation was recommenced, the same fractionating column being used throughout. This oil had previously been investigated by Lachowicz (*Annalen*, 1883, 220, 188), who concluded that the proportion of naphthenes present was greater than in American petroleum, although considerably less than in Caucasian naphtha; there seemed, therefore, reasonable hope that pure hexamethylene might be obtained from it by repeated fractional distillation, and this expectation has been realised. After about nine months' work, a fraction was obtained boiling constantly at 80.8° (corr.) and having the sp. gr. 0.7903 at 0°/4°; this fraction was set apart for the determination of certain physical constants, whilst the others, boiling within a range of 1° were used for the preparation of derivatives, of which the following were obtained. The monochloride,  $C_6H_{11}Cl$ ; dichloride,  $C_6H_{10}Cl_2$ ; trichloride,  $C_6H_9Cl_3$ ; and tetrachloride,  $C_6H_8Cl_4$ ; the monobromide,  $C_6H_{11}Br$ ; dibromide,  $C_6H_{10}Br_2$ ; and tetrabromide,  $C_6H_8Br_4$ ; dihydrobenzene,  $C_6H_8$ ; tetrahydrobenzene,  $C_6H_{10}$ ; chlorodihydrobenzene,  $C_6H_7Cl$ ; chlorohydroxyhexamethylene,  $C_6H_{10}OH \cdot Cl$ ; (*Proc. Chem. Soc.*, 1897, p. 161; 1898, p. 103). Of these substances, the following have been prepared synthetically by Baeyer: the monobromide, dibromide, and tetrabromide, dihydrobenzene and tetrahydrobenzene. The agreement between the properties is, on the whole, satisfactory, as will be seen from the following comparison (p. 934), especially when it is remembered that the quantities of the substances obtained by the synthetical methods were very small.

It may be noted that, in an earlier paper, Baeyer gives the boiling point of dihydrobenzene as about 81.5°.

Dr. W. H. Perkin, sen., has very kindly determined the magnetic

	B. p.		M. p.	
	Baeyer.	E. C. F.	Baeyer.	E. C. F.
Hexamethylene .....	79— 79·5°	80·8°		
Tetrahydrobenzene.....	82— 84	82·3		
Dihydrobenzene .....	84— 86	81—82		
Monobromhexamethylene .....	165—166	162—163		
Dibromhexamethylene ..... {	215—220	145—146		
	(713 mm.)	(100 mm.)		
Tetrabromhexamethylene .....			184—185°	185°

rotation of hexamethylene and of tetrahydrobenzene; unfortunately, the amount of dihydrobenzene obtained was not sufficient for the purpose. He has, however, determined the index of refraction and the specific and molecular refractions of all three hydrocarbons, and the results are tabulated on p. 946 and compared with the numbers obtained by Brühl.

The same constants have been determined by Dr. Perkin for monochlor- and dichlor-hexamethylene and for monobromhexamethylene.

#### *Hexamethylene from American Petroleum.*

Twenty-five pounds of American light petroleum having the sp. gr. 0·680 were procured and distilled in 10 successive portions from a can of about 5 litres capacity. No correction was made during the first few distillations for the barometric pressure, as it would have been negligible compared with the alteration of temperature caused by slight variations in the rate of distillation. The first drops distilled over at 16°, but all below 28° and above 95° was rejected. After nine distillations, extending over two months, the fractions were freed from aromatic hydrocarbons by nitrating the latter; they were first shaken three times in separating funnels with sulphuric acid, and then with two or three times their volume of a mixture of nitric and sulphuric acids, in the proportion of 3:10 by weight, with which they were left in contact for some hours. The mixed acids were then separated from the hydrocarbon, and poured into a large volume of water, when crystals were obtained from several of the fractions; this treatment was repeated until no turbidity was produced on diluting the mixed acids with water. The crystals, when collected and recrystallised five times from methylated spirits and water, and then once from water, melted at 89·6°, showing that they were pure metadinitrobenzene; the greatest quantity was obtained from the lowest fraction, which boiled at 68—70°, and decreasing amounts were

obtained from successive fractions up to 74—77.5°. From the higher fractions, no crystals were obtained, showing that benzene was apparently the only aromatic hydrocarbon present. The fact that this substance, when mixed with the paraffins, distils over far below its true boiling point had already been observed by Dr. Young. The fractions were next treated three times with about twice their volume of sulphuric acid, the operation lasting about an hour, and after washing twice with water, they were shaken twice with a strong solution of caustic potash. They were again washed three times with water, and then dehydrated with phosphoric anhydride. Each fraction was then distilled separately into its old flask from a distilling flask containing roughly powdered caustic potash; the operation was repeated with fresh potash, and the fractional distillation was then continued. After the tenth distillation, the specific gravity of some of the fractions was taken, the highest being 0.7513 at 0°/4° for fraction 80—83°. After 15 distillations, the sp. gr. of the purest fraction was 0.7621, and after 33, the highest sp. gr. was 0.7722, namely, that of the fraction 80.55—80.65°. This fraction gave, on analysis, the following numbers, which agree fairly well with those required for hexamethylene.

0.0716 gave 0.2239 CO<sub>2</sub> and 0.0931 H<sub>2</sub>O. C = 85.22; H = 14.44.

C<sub>6</sub>H<sub>12</sub> requires C = 85.71; H = 14.29 per cent.

As a proof that the substance was hexamethylene itself, and not one of its isomerides, it was oxidised with fuming nitric acid, when it yielded adipic acid, as had been previously shown by Markownikoff (*Ber.*, 1897, 30, 975) in the case of hexanaphthene from Caucasian petroleum.

Although the specimen of hexamethylene obtained was not entirely free from paraffins, it was necessary to stop the distillation at the above stage, as the quantities were so small as to render further purification of the substance impossible; the fractions boiling between 80.25° and 80.65° were used in the following experiments.

#### *Action of Chlorine.*

The hydrocarbon (10 grams) was placed in a reflux apparatus, together with iron filings (0.5 gram), and exposed to sunlight while a current of dry chlorine was passed through the liquid; in less than half an hour, chemical action began, the liquid became hot, and hydrogen chloride was evolved in abundance. After about 4 hours, the action was interrupted, the product washed successively with sodium carbonate solution and water, and dried over calcium chloride. When about

70 grams of hexamethylene had been chlorinated in this way, the dried product was distilled under reduced pressure; no monochlorhexamethylene was obtained, but after repeated fractional distillation under a pressure of 30 mm. a fraction boiling at 110—115° (30 mm.) was obtained, consisting chiefly of *dichlorhexamethylene*,  $C_6H_{10}Cl_2$  a substance which is described in greater detail on p. 943.

0.1242 gave 0.2094  $CO_2$  and 0.0634  $H_2O$ . C = 45.98; H = 5.67.

0.2881 „ 0.5642 AgCl. Cl = 48.34.

$C_6H_{10}Cl_2$  requires C = 47.12; H = 6.54. Cl = 46.34 per cent.

The oils boiling above 115° (at 30 mm.) were subjected to repeated careful fractionation under reduced pressure, when two fractions of fairly constant boiling point were obtained, one boiling at 135—140° (at 30 mm.) and the other at 160—165° (at 30 mm.). The former consisted chiefly of *trichlorhexamethylene*,  $C_6H_9Cl_3$ , and gave the following numbers on analysis.

0.1240 gave 0.1706  $CO_2$  and 0.0585  $H_2O$ . C = 37.52; H = 5.24.

0.2512 „ 0.5930 AgCl. Cl = 58.27.

$C_6H_9Cl_3$  requires C = 38.46; H = 4.81; Cl = 56.73 per cent.

The higher boiling fraction was chiefly composed of *tetrachlorhexamethylene*  $C_6H_8Cl_4$ , an analysis giving the following results.

0.1213 gave 0.1406  $CO_2$  and 0.0377  $H_2O$ . C = 31.61; H = 3.45.

0.2669 „ 0.7029 AgCl. Cl = 65.01.

$C_6H_8Cl_4$  requires C = 32.49; H = 3.61; Cl = 63.90 per cent.

Both the above fractions were heavy, pale yellow oils, which distilled without decomposition under a pressure of 30 mm., and on long standing deposited crystals, but not in sufficient quantity for analysis. The fraction consisting chiefly of trichlorhexamethylene was heated with alcoholic potash on the water bath for some hours in a reflux apparatus. Potassium chloride separated, and the product was extracted with ether, washed, dried, and fractionated after distilling off the ether. As it seemed probable that the small quantity of liquid boiling below 90° might contain benzene, formed from trichlorhexamethylene by the removal of 3HCl, it was treated with a mixture of nitric and sulphuric acids. The product had the odour of nitrobenzene, and on extracting with ether, reducing, &c., aniline was detected by its odour, and by the purple coloration produced by bleaching powder.

Besides benzene, a considerable quantity of a substance boiling at 135—140° was isolated from the product of the action of alcoholic potash on trichlorhexamethylene; this consisted of *chlorodihydrobenzene*,  $C_6H_7Cl$ , formed by the removal of 2HCl from trichlorhexamethylene.



0.0970 gave 0.2228  $\text{CO}_2$  and 0.0516  $\text{H}_2\text{O}$ .  $\text{C} = 63.20$  ;  $\text{H} = 5.91$ .

0.1684 „ 0.2065  $\text{AgCl}$ .  $\text{Cl} = 30.36$ .

$\text{C}_6\text{H}_7\text{Cl}$  requires  $\text{C} = 62.93$  ;  $\text{H} = 6.12$  ;  $\text{Cl} = 30.95$  per cent.

The action of alcoholic potash on dichlorhexamethylene and tetrachlorhexamethylene was also investigated, but in both cases the action was a complicated one, and the amount of material at my disposal was, unfortunately, too small to allow of a separation being effected.

In view of the statements of both Markownikoff (*Ber.*, 1897, 30, 1222) and Zelinsky (*Ber.*, 1897, 30, 1532) that methylpentamethylene is obtained by heating derivatives of hexamethylene with concentrated hydriodic acid, it seemed to be of interest to ascertain whether the hydrocarbon itself would undergo isomeric change under these conditions. It was therefore heated in a sealed tube, with five times the volume of hydriodic acid and a little amorphous phosphorus for 3 hours at temperatures ranging from  $160^\circ$  to  $270^\circ$ . The product, after being washed and dried, boiled almost constantly at  $80^\circ$ , whereas methylpentamethylene boils at  $70$ — $71^\circ$ . Hexamethylene, therefore, remains unchanged under these conditions, being apparently more stable in this respect than some of its derivatives.

#### *Hexamethylene from Galician Petroleum.*

Twenty-five kilograms of Galician oil of low boiling point were procured from Kahlbaum and distilled in 14 portions from a tin of about one gallon capacity, using the same fractionating column as before. As one distillation alone of this quantity extended over nearly three months, all the liquid boiling below  $65^\circ$  and above  $96^\circ$  was discarded ; after 12 distillations of the fractions retained, they were treated with a mixture of nitric and sulphuric acids to remove the benzene, which was found in all the fractions up to and including  $79.7$ — $80.7^\circ$ , but not in the higher fractions, the treatment with the acids being repeated until all traces of benzene were removed. The fractions were then washed and dried as before, and distilled over potash into their old flasks, after which the fractional distillation was continued. After the fourteenth distillation, the specific gravity of the fractions was taken and the results are given in the table on page 938. The column headed  $\Delta w/\Delta T$  represents the weight in grams of each fraction divided by its temperature range, and thus gives a measure of the relative purity of the fractions.\*

A fractional distillation of the portion boiling at  $80.7$ — $81^\circ$  was then carried out separately, as the time required to go through the

\* See S. Young, *Phil. Mag.*, Jan., 1894, p. 25.



Fraction.	Weight $\Delta w$	$\frac{\Delta w}{\Delta T}$	Sp. gr. at 0°/4°.
71·5—74°	134	53·6	—
74 —76	75	37·5	0·7529
76 —78·5	166	66·4	0·7648
78·5—79·5	75	75	0·7720
79·5—80·2	176	251·4	0·7756
80·2—80·7	211	422	0·7817
80·7—81·0	322	1073·3	0·7834
81·0—81·5	219	538	0·7819
81·5—83·2	171	100·5	0·7764
83·2—87·2	119	31·3	0·7549

whole fractionation until a pure substance was obtained would have been too great. Four of the remaining fractions, namely, the two boiling nearest on each side of the fraction 80·7—81° were subsequently used in the preparation of derivatives.

After 11 distillations, a fraction boiling apparently constantly at 80·7° was obtained, and the specific gravity of this fraction and those on either side of it were taken.

Fraction.	Sp. gr. at 0°/4°.
80·65—80·7°	0·7846
80·7	0·7878
80·7—80·75	0·7899

The higher specific gravity of the last fraction showed that pure hexamethylene had not yet been obtained, and the distillation was therefore continued. In addition to the difficulty of reading accurately to within a twentieth of a degree, considerable trouble was experienced, owing to the fact that the constant of the variation of the boiling point with the pressure was not known for hexamethylene, and a slight error in this constant would make an appreciable difference in determining the true boiling point. It was found that the most concordant results were obtained by assuming that a change of pressure of 1 mm. corresponded with a difference of 0·04° in the boiling point. Three more distillations were carried out, and then a fraction consisting of 37 grams was obtained which boiled constantly at 80·8° and had a higher specific gravity than those on either side of it.

Fraction.	Sp. gr. at 0°/4°.
80·75—80·8	0·7881
80·8	0·7903
80·8—80·85	0·7896

The liquid boiling constantly at 80·8° was analysed and the results obtained indicate that it was pure hexamethylene.

0.1311 gave 0.4110 CO<sub>2</sub> and 0.1691 H<sub>2</sub>O. C = 85.50; H = 14.34.

C<sub>6</sub>H<sub>12</sub> requires C = 85.71; H = 14.29 per cent.

Hexamethylene is a colourless, volatile oil with a pleasant odour resembling that of light petroleum. It is not attacked by bromine in the cold, and is not oxidised by potassium permanganate solution. The specific gravities at different temperatures, the magnetic rotation, and the refraction constants of this specimen were determined by Dr. W. H. Perkin, sen., with the following results.

*Specific gravity.*  $d\ 4^{\circ}/4^{\circ} = 0.7865$ ;  $d\ 10^{\circ}/10^{\circ} = 0.7812$ .

$d\ 15^{\circ}/15^{\circ} = 0.7771$ ;  $d\ 20^{\circ}/20^{\circ} = 0.7731$ ;  $d\ 25^{\circ}/25^{\circ} = 0.7694$ .

*Magnetic rotation* (mean of two determinations).

$t$	Sp. rot.	Mol. rot.
16.1°	0.9752	5.754

This rotation is very much lower than was to be expected. In ring compounds, the value for CH<sub>2</sub> is usually nearly normal, namely, 1.023. Hexamethylene would therefore be expected to have a molecular rotation of about  $1.023 \times 6 = 6.128$  or 0.374 higher than that given by the product examined.

\* *Refraction*,  $t = 17.4^{\circ}$ ;  $d\ 17.4^{\circ}/4^{\circ} = 0.7742$ .

	Index of refraction	Sp. refraction		Mol. refraction.	
	$\mu$ .	$\frac{\mu-1}{d}$	$\frac{\mu^2-1}{\mu^2+2} \cdot \frac{1}{d}$	$\frac{\mu-1}{d} \cdot P$ .	$\frac{\mu^2-1}{\mu^2+2} \cdot \frac{P}{d}$ .
A.....	1.41977	0.54217	0.32671	45.542	27.444
Li .....	1.4218	0.54480	0.32810	45.762	27.560
H <sub>a</sub> .....	1.42211	0.54520	0.32831	45.797	27.578
Na .....	1.42446	0.54823	0.32991	46.051	27.713
H <sub><math>\beta</math></sub> .....	1.42960	0.55488	0.33340	46.610	28.003
H <sub><math>\gamma</math></sub> .....	1.43391	0.56044	0.33631	47.077	28.292

The calculated molecular refraction for H<sub>a</sub> is 45.653, the above being 45.797; the difference is not very large, but is in the opposite direction to the rotation.

The agreement with the numbers obtained by Brühl is very good; a table of comparison is given on p. 946.

\* In this and all other cases, the specific and molecular refractions have been calculated according to the formulae  $\frac{\mu^2-1}{\mu^2+2} \cdot \frac{1}{d}$  and  $\frac{\mu^2-1}{\mu^2+2} \cdot \frac{P}{d}$  from Dr. Perkin's determinations of  $\mu$  and  $d$ , for the sake of comparison with the numbers obtained by Brühl.

*Derivatives of Hexamethylene from Galician Petroleum.*

*Monochlorhexamethylene*,  $C_6H_{11}Cl$ , and its conversion into *Tetrahydrobenzene*,  $C_6H_{10}$ .—Monochlorhexamethylene was obtained together with dichlorhexamethylene by passing a current of dry chlorine into hexamethylene in the cold, in diffused daylight. An attempt to chlorinate in the dark was made in order to see whether in this way the action of the chlorine would stop after the formation of a monochloro-derivative, but it proved unsuccessful, hexamethylene remaining almost unchanged. It had already been found (p. 935) that application of heat or the addition of chlorine carriers gave rise to the formation almost exclusively of higher substitution products such as di-, tri-, and tetra-chlorhexamethylene. When chlorine is passed into hexamethylene in the cold, it dissolves, in the first instance forming a yellow solution, then, at a certain point, combination begins, heat is developed and hydrogen chloride is evolved. If from this point the gas is passed slowly for about 3 hours, a good yield of the monochloride is obtained. Similar observations were made by Schorlemmer (*Annalen*, 1877, 188, 250) in the case of the chlorination of isoheptane, the action indeed taking place in the same way. The product was washed with sodium carbonate solution, and then with water and dried over calcium chloride.

After repeated fractional distillations with a Glinsky column, a sample of monochlorhexamethylene was obtained boiling at  $141.3\text{--}141.6^\circ$  (768 mm.) and having a sp. gr. = 0.9991 at  $0^\circ/0^\circ$ .

0.1758 gave 0.2130 AgCl.  $Cl = 29.85$ .

$C_6H_{11}Cl$  requires  $Cl = 29.86$  per cent.

Monochlorhexamethylene is a colourless oil with a characteristic odour; it is an unstable substance readily losing a molecule of hydrogen chloride and yielding tetrahydrobenzene. It distils, however, unchanged when pure. It dissolves in strong sulphuric acid with evolution of heat, giving a deep red solution. The sp. gr., magnetic rotation, and refraction experiments gave the following results.

*Specific gravity.*  $d\ 4^\circ/4^\circ = 0.9897$ ;  $d\ 10^\circ/10^\circ = 0.9842$ ;  
 $d\ 15^\circ/15^\circ = 0.9800$ ;  $d\ 20^\circ/20^\circ = 0.9762$ ;  $d\ 25^\circ/25^\circ = 0.9725$ .

*Magnetic rotation* (twice determined).

	<i>t</i> .	Sp. rot.	Mol. rot.
Average .....	15.8	1.1125	7.478

This molecular rotation, like that of hexamethylene, is somewhat lower than the calculated, if the value of chlorine replacing hydrogen

is taken as 1.558, namely, that which it has in the paraffin series, thus,

$$6\text{CH}_2 = 6 \times 1.023 = 6.138$$

$$\text{Cl replacing H} = 1.558$$

Calculated rotation of monochlorohexamethylene = 7.696

Refraction,  $t = 18^\circ$ ;  $d \ 18^\circ/4^\circ = 0.9765$ .

	Index of re- fraction.	Sp. refraction.		Mol. refraction.	
	$\mu$	$\frac{\mu-1}{d}$	$\frac{\mu^2-1}{\mu^2+2} \cdot \frac{1}{d}$	$\frac{\mu-1}{d} \cdot P$	$\frac{\mu^2-1}{\mu^2+2} \cdot \frac{P}{d}$
A .....	1.45053	0.46138	0.27549	54.673	32.563
Li .....	1.45267	0.46358	0.27661	54.934	32.695
H <sub>a</sub> .....	1.45313	0.46404	0.27686	54.989	32.725
Na .....	1.45552	0.46649	0.27812	55.279	32.874
H <sub>s</sub> .....	1.46153	0.47264	0.28128	56.008	33.248
H <sub>y</sub> .....	1.46644	0.47767	0.28286	56.604	33.552

This result is a good deal higher than the calculated, thus,

Molecular refraction for H<sub>a</sub> found = 54.989

Calculated 54.170

Difference = 0.819

*Tetrahydrobenzene*, C<sub>6</sub>H<sub>10</sub>, is very readily prepared from monochlorohexamethylene, being formed when the latter is heated with quinoline or alcoholic potash, and in smaller quantity when heated with moist silver oxide or even with silver acetate or silver nitrite, the best yield being obtained by heating with quinoline for 7 or 8 hours in a reflux apparatus. On subjecting the product to careful fractional distillation without previous washing with acid, a fraction was finally obtained boiling constantly at 82.3° (764 mm.).

An analysis of the freshly distilled substance gave the following numbers.

0.1230 gave 0.3947 CO<sub>2</sub> and 0.1503 H<sub>2</sub>O. C = 87.50; H = 12.22.

C<sub>6</sub>H<sub>10</sub> requires C = 87.80; H = 12.20 per cent.

It yielded a liquid dibromide (p. 948) and a crystalline nitrosochloride, and its alcoholic solution was coloured yellow on warming with concentrated sulphuric acid as stated by Baeyer (*Ber.*, 1893, 26, 230).

Determinations of the specific gravity, magnetic rotation, and refraction were made by Dr. Perkin. The specimen sent him distilled in

the first instance constantly at  $82.3^{\circ}$  (764 mm.), but after standing for some days, it was found that it did not evaporate completely when placed on bibulous paper, but left an oily stain.

*Specific gravity.*  $d\ 4^{\circ}/4^{\circ} = 0.8244$ ;  $d\ 10^{\circ}/10^{\circ} = 0.8188$ ;  
 $d\ 15^{\circ}/15^{\circ} = 0.8149$ ;  $d\ 20^{\circ}/20^{\circ} = 0.8110$ ;  $d\ 25^{\circ}/25^{\circ} = 0.8072$ .

	<i>t.</i>	Sp. rot.	Mol. rot.
<i>Magnetic rotation.</i>	$15^{\circ}$	1.1439	6.395

The specimen was then redistilled, when the chief fraction came over at  $82.3^{\circ}$ ; the temperature then gradually rose, until a gummy product was left in the retort, and this, on further heating, seemed to undergo decomposition, some drops of water condensing in the neck of the distilling flask, a fact which seems to indicate that the gummy product contained a product of the oxidation of the hydrocarbon. The tendency of unsaturated cyclic hydrocarbons to become oxidised to thick gummy substances in presence of air has been noted by Markownikoff (*Annalen*, 1898, 301, 158).

The fraction boiling at  $82.3^{\circ}$  was then examined.

*Specific gravity.*  $d\ 20^{\circ}/20^{\circ} = 0.7995$ ;  $d\ 25^{\circ}/25^{\circ} = 0.7956$ .

The expansions given by these density determinations are practically the same as for the undistilled product, but the densities are about 0.0154 lower.

*Magnetic rotation of recently distilled product.*

<i>t.</i>	Sp. rot.	Mol. rot.
$16.8^{\circ}$	1.1198	6.392

It will be seen that the specific rotation is much lower than in the original product, but owing to the change in density, this is counter-balanced in the calculation for the molecular rotation, which comes out much the same as before.

The molecular rotation of this compound is very low. If compared with that of hexamethylene, it will be seen that the difference is not much greater than it should be for the difference in composition of  $H_2$ , namely, 0.508, whereas it would be expected to be this *plus* the difference for unsaturation, which is generally about 1.112.

$$\begin{array}{rcl} \text{Tetrahydrobenzene} & = & 6.392 \\ \text{Hexamethylene} & = & 5.754 \\ \hline & & 0.638 \end{array}$$

It is certainly very remarkable that the magnetic rotation of hexamethylene and tetrahydrobenzene should be so low, unlike that of any other hydrocarbons which Dr. Perkin has as yet examined.



Refraction of redistilled specimen.  $t = 14.4$ ;  $d_{14.4/4^\circ} = 0.79934$ .

	Index of re- fraction.	Sp. refraction.		Mol. refraction.	
	$\mu$ .	$\frac{\mu-1}{d}$ .	$\frac{\mu^2-1}{\mu^2+2} \cdot \frac{1}{d}$ .	$\frac{\mu-1}{d} \cdot P$ .	$\frac{\mu^2-1}{\mu^2+2} \cdot \frac{P}{d}$ .
H <sub>a</sub> .....	1.43998	0.55043	0.32970	45.135	27.035
H <sub>s</sub> .....	1.44943	0.56224	0.33583	46.104	27.538
H <sub>y</sub> .....	1.45507	0.56930	0.33947	46.683	27.837

The molecular refraction of the redistilled specimen is not far from that calculated for C<sub>6</sub>H<sub>10</sub> with one ethylene linking, but is rather low.

$$C_6 = 30.000$$

$$H_{10} = 13.000$$

$$\text{Ethylene linking} = 2.300$$

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$$45.300$$

$$\text{Found } 45.135$$

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$$\text{Difference} = 0.165$$

*Dichlorhexamethylene*, C<sub>6</sub>H<sub>10</sub>Cl<sub>2</sub>, and its conversion into *Dihydrobenzene*, C<sub>6</sub>H<sub>8</sub>.—In the course of the preparation of monochlorhexamethylene, a considerable quantity of a substance of higher boiling point was obtained; this was submitted to fractional distillation, when the largest quantity boiled at 190—195°. On exposure to air, it became rapidly coloured, but on further fractionation, about 15 grams of a colourless liquid was obtained boiling at 193—194°. This fraction gave the following numbers on analysis.

0.2251 gave 0.4204 AgCl. Cl = 46.04.

C<sub>6</sub>H<sub>10</sub>Cl<sub>2</sub> requires Cl = 46.30 per cent.

Dichlorhexamethylene is a heavy, colourless oil with a penetrating odour, and, like monochlorhexamethylene, dissolves in strong sulphuric acid, forming a deep red solution. Determinations were made by Dr. Perkin of its specific gravity, magnetic rotation, and refraction.

*Specific gravity.*  $d_{4^\circ/4^\circ} = 1.1777$ ;  $d_{10^\circ/10^\circ} = 1.1720$ ;  
 $d_{15^\circ/15^\circ} = 1.1673$ ;  $d_{20^\circ/20^\circ} = 1.1638$ ;  $d_{25^\circ/25^\circ} = 1.1603$ .

	$t$ .	Sp. rot.	Mol. rot.
<i>Magnetic rotation.</i>	16.6°	1.2224	8.906

The calculated value of dichlorhexamethylene may be obtained as follows.

$$6\text{CH}_2 = 6 \times 1.023 = 6.138$$

$$2\text{Cl replacing } 2\text{H} = 2 \times 1.558 = 3.116$$

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$$\text{Calc. rotation of dichlorhexamethylene} = 9.254$$

$$\text{Refraction. } t = 16.6^\circ; d_{16.6^\circ/4^\circ} = 1.670.$$

	Index of re- fraction.	Sp. refraction.		Mol. refraction.	
	$\mu$ .	$\frac{\mu-1}{d}$ .	$\frac{\mu^2-1}{\mu^2+2} \cdot \frac{1}{d}$ .	$\frac{\mu-1}{d} \cdot P$ .	$\frac{\mu^2-1}{\mu^2+2} \cdot \frac{P}{d}$ .
A.....	1.48274	0.41365	0.17094	63.288	26.050
Li.....	1.48517	0.41574	0.17167	63.608	26.162
H <sub>a</sub> .....	1.48556	0.41607	0.17179	63.659	26.180
Na.....	1.48862	0.41692	0.17271	64.060	26.321
H <sub><math>\beta</math></sub> .....	1.49467	0.42388	0.17452	64.853	26.598
H <sub><math>\gamma</math></sub> .....	1.50189	0.43006	0.17668	64.800	26.926

On comparing the value obtained with that calculated for H<sub>a</sub>, we have the following result.

Found 63.659

Calc. 62.740

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Difference = 0.919

This compound, then, gives higher refraction values than were to be expected.

The oil boiling above 194° was submitted to careful fractional distillation, and a considerable quantity of liquid was obtained boiling very constantly between 201° and 202° and giving the following numbers on analysis.

0.1990 gave 0.3823 AgCl. Cl = 47.28.

C<sub>6</sub>H<sub>10</sub>Cl<sub>2</sub> requires Cl = 46.30.

Possibly this oil may contain a dichlorhexamethylene which is isomeric with the dichlorhexamethylene boiling at 193—194°, but the quantity of material at my disposal was not sufficient to decide this point.

*Dihydrobenzene*, C<sub>6</sub>H<sub>8</sub>, was obtained by distilling dichlorhexamethylene with quinoline; in this case, it was found that the yield was not increased by prolonged heating of the mixture before distillation. The product, after repeated fractional distillation, yielded a fraction boiling

at 81—82°; this was redistilled just before the analysis, when the following result was obtained.

0.2806 gave 0.9274 CO<sub>2</sub> and 0.2527 H<sub>2</sub>O. C = 90.14; H = 10.00.

C<sub>6</sub>H<sub>8</sub> requires C = 90.00; H = 10.00 per cent.

Dihydrobenzene is a light, colourless oil with a peculiar odour resembling that of tetrahydrobenzene, and very readily undergoes oxidation. The vapour turns potassium permanganate solution brown (Baeyer, *Ber.*, 1893, 26, 230), and on standing it takes up oxygen from the air and is converted into a thick, syrupy liquid. At first, a heavy layer is formed at the bottom of the tube, and this gradually spreads up through the liquid until, finally, the tube may be inverted without spilling its contents. The liquid boiling at 81—82° was sent to Dr. W. H. Perkin, sen., and he determined the specific gravity and the refraction constants. The specimen sent him, like that of tetrahydrobenzene, had undergone some change by keeping, as it did not evaporate regularly on blotting paper. Unfortunately, there was not enough to allow of the determination of the magnetic rotation, so that in this respect its relationship to benzene and tetrahydrobenzene could not be ascertained.

*Specific gravity* of redistilled specimen.  $d_{15^\circ/15^\circ} = 0.84987$ .

*Refraction* of redistilled specimen.  $t = 15.5^\circ$ ;  $d_{15.5^\circ/4^\circ} = 0.84785$ .

	Index of refraction.	Sp. refraction.		Mol. refraction.	
	$\mu$ .	$\frac{\mu-1}{d}$ .	$\frac{\mu^2-1}{\mu^2+2} \cdot \frac{1}{d}$ .	$\frac{\mu-1}{d} \cdot P$ .	$\frac{\mu^2-1}{\mu^2+2} \cdot \frac{P}{d}$ .
H <sub>a</sub> .....	1.47254	0.55734	0.32681	44.587	26.145
H <sub><i>s</i></sub> .....	1.48687	0.57424	0.33711	45.939	26.969
H <sub><i>v</i></sub> .....	1.49589	0.58488	0.34389	46.790	27.511

The refraction of this compound does not differ largely from the calculated value with two ethylene linkings, although it is somewhat lower.

$$C_6 = 30.000$$

$$H_8 = 10.400$$

$$\text{Two ethylene linkings} = 4.600$$

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$$45.000$$

$$\text{Found} = 44.587$$

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$$\text{Difference} = 0.413$$

It may be interesting here to give a table comparing the refraction constants of hexamethylene, tetrahydrobenzene, and dihydrobenzene, as determined by Dr. Perkin from the author's specimens with those of the same hydrocarbons determined by Brühl from specimens obtained synthetically by Baeyer.

	Sp. gr. d.		Index of refraction, $\mu$ .		Sp. refraction. $\frac{\mu_a^2-1}{\mu_a^2+2} \cdot \frac{1}{d}$		Mol. refraction. $\frac{\mu_a^2-1}{\mu_a^2+2} \cdot \frac{P}{d}$	
	Brühl.	Perkin.	Brühl.	Perkin.	Brühl.	Perkin.	Brühl.	Perkin.
Benzene, $C_6H_6$ .....	0·8799 (20°/4°)		1·4967		0·3324		25·93	
Dihydrobenzene, $C_6H_8$ .....	0·8478 (20°/4°)	0·84785 (15·5°/4°)	1·4699	1·47254	0·3291	0·32681	26·33	26·145
Tetrahydrobenzene, $C_6H_{10}$	0·8102 (20°/4°)	0·79934 (14·4°/4°)	1·4435	1·43908	0·3277	0·32970	26·87	27·035
Hexamethylene, $C_6H_{12}$ ....	0·790 (20°/4°)	0·7742 (17·4°/4°)	1·426	1·42211	0·3255	0·32831	27·56	27·578

The specific gravity of the hexamethylene prepared by Baeyer is considerably higher than that of the specimen obtained during the present research, but the agreement between the refraction determinations is very good in the case of all three hydrocarbons. The constants for benzene are appended for the sake of comparison.

*Dispersion of the hydrocarbons.*

	Mol. refraction for $H_y-H_x$ .	Dispersion.
Hexamethylene	$= 28·292 - 27·578$	$= 0·714$
Tetrahydrobenzene	$= 27·837 - 27·035$	$= 0·802$
Dihydrobenzene	$= 27·511 - 26·145$	$= 1·366$

*Monobromhexamethylene*,  $C_6H_{11}Br$ .—Many attempts were made in the first instance to prepare this substance by the direct bromination of hexamethylene both with and without the aid of a bromine carrier, but the results proved unsatisfactory, as the products on distillation always decomposed at a comparatively low temperature, so that purification by fractionation was impossible. The behaviour of the hydrocarbon in this respect is very similar to that of normal hexane and isoheptane, as Schorlenmer was only able to obtain an exceedingly poor yield of the secondary bromide from these hydrocarbons by direct bromination, much loss being caused by decomposition (*Annalen*, 1877, 188, 250). Ultimately, monobromhexamethylene was obtained in a pure state by the addition of hydrogen bromide to tetrahydrobenzene. In the first experiments, the hydrocarbon was dissolved in an acetic acid solution of hydrogen bromide, and after standing all night and then warming for a short time on the water bath at 60°, it was mixed with water and the heavy oil extracted with ether, washed with sodium carbonate solution, and dried over calcium chloride. On distilling the product, it was found that, although most of the oil dis-

tilled fairly constantly at 163—164°, a small quantity of a substance of higher boiling point was present which smelt like pear-drops and was evidently the corresponding acetate. Different specimens of the monobromide prepared in this way, when analysed, gave the bromine always 3 to 4 per cent. too low. Tetrahydrobenzene was then placed in a reflux apparatus with 4 or 5 times its volume of aqueous hydrobromic acid saturated at 0°; no action took place in the cold, but on warming on a water bath, the colour of the hydrocarbon changed to deep violet and after about 4 hours the action was complete. On pouring the product into water, the heavy monobromide sank to the bottom as a brown oil which was extracted with ether, washed, dried, and distilled; the greater part of the liquid boiled with slight decomposition at 162—163°, and a bromine determination gave the following result.

0.1665 gave 0.1917 AgBr. Br = 49.00.

$C_6H_{11}Br$  requires Br = 49.08 per cent.

Monobromhexamethylene is a heavy, colourless oil which readily turns brown on exposure to air; the odour is penetrating, and its vapour has a slightly irritating effect on the eyes. It is very readily acted on by alcoholic potash, tetrahydrobenzene being obtained. The specimen sent to Dr. W. H. Perkin, sen., was too dark in colour for the determination of the magnetic rotation, and when distilled it gave off a little hydrobromic acid and soon became coloured again.

*Specific gravity.*  $d\ 4^\circ/4^\circ = 1.3406$ ;  $d\ 10^\circ/10^\circ = 1.33415$ .

$d\ 15^\circ/15^\circ = 1.3290$ ;  $d\ 20^\circ/20^\circ = 1.3240$ ;  $d\ 25^\circ/25^\circ = 1.3188$ .

The refraction of the sample was determined for three lines only, as it was too dark to allow of others being measured.

*Refraction*,  $t = 14.6^\circ$ ;  $d\ 14.6^\circ/4^\circ = 1.3264$ .

	Index of refraction.	Sp. refraction.		Mol. refraction.	
	$\mu$ .	$\frac{\mu-1}{d}$ .	$\frac{\mu^2-1}{\mu^2+2} \cdot \frac{1}{d}$ .	$\frac{\mu-1}{d} \cdot P$ .	$\frac{\mu^2-1}{\mu^2+2} \cdot \frac{P}{d}$ .
Li .....	1.49177	0.37077	0.21864	60.435	35.638
H <sub>a</sub> .....	1.49255	0.37135	0.21894	60.530	35.686
Na .....	1.49564	0.37368	0.22010	60.910	35.876

This compound, like the corresponding chlorine derivative, gives higher numbers than the calculated, thus,



Molecular refraction for  $H_a$  found = 60.530

Calculated = 59.690

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 Difference = 0.840

*Dibromhexamethylene*,  $C_6H_{10}Br_2$ , was obtained by the action of bromine on tetrahydrobenzene in ethereal solution. The flask was cooled with water and the bromine added drop by drop, when rapid decolorisation took place, heat being evolved; as soon as a drop of bromine produced a permanent coloration in the solution, it was washed with dilute caustic soda solution and dried, the ether was distilled off, and the dibromide distilled under reduced pressure. It boiled at 145—146° under a pressure of 100 mm.

0.3228 gave 0.5028 AgBr. Br = 66.22.

 $C_6H_{10}Br_2$  requires Br = 66.12 per cent.

Dibromhexamethylene, when pure, is a heavy, colourless oil, but it rapidly decomposes on exposure to air, becoming very dark. It is readily acted on by alcoholic potash, yielding dihydrobenzene.

*Tetrabromhexamethylene*,  $C_6H_8Br_4$ , was obtained in a crystalline form by the action of bromine on dihydrobenzene in ethereal solution; on adding a drop of bromine to the solution, it was instantly decolorised, and white crystals separated. These were washed with ether and dried, when they melted at 184° (Baeyer 184—185°).

0.1317 gave 0.2572 AgBr. Br = 79.83.

 $C_6H_8Br_4$  requires Br = 80.00 per cent.

*Chlorhydroxyhexamethylene*,  $C_6H_{10}Cl.OH$ .—A solution of hypochlorous acid, obtained by passing chlorine into a mixture of ice and water containing freshly precipitated mercuric oxide in suspension, was shaken with tetrahydrobenzene. Heat was evolved, and the oil which formed and settled at the bottom of the flask was distilled with steam, separated from the aqueous layer, and dehydrated with calcium chloride.

0.1417 gave 0.1542 Cl. Cl = 26.86.

 $C_6H_{10}Cl.OH$  requires Cl = 26.34 per cent.

The liquid was pale yellow, had a characteristic odour, and decomposed on distillation. On treating it with zinc dust and acetic acid, much heat was evolved, but the final product still contained chlorine, and the quantity of substance was insufficient to repeat the reduction so as to obtain the corresponding alcohol.

A fractional distillation of the portion of Galician petroleum boiling below 70° was undertaken, in order, if possible, to isolate pure penta-

methylene from the oil. It appears, however, not to be present in quantity sufficient to enable this to be done without a very large expenditure of time, and if any further attempts in this direction are made, the source used must be Caucasian naphtha.

I wish to express my sincere thanks to Dr. W. H. Perkin, sen., for his courtesy in permitting me to include in this paper his determinations of the specific gravity, magnetic rotation, and optical constants of the substances obtained; to Professor S. Young for the use of the fractionating column, without which the isolation of pure hexamethylene would have been impossible, and particularly to Professor W. H. Perkin for his kind advice and help during the course of this research, which has been carried out under his guidance at Owens College. I am also greatly indebted to him for the analyses of hexamethylene, tetrahydrobenzene, and dihydrobenzene which he carried out after I left Manchester.

NOTE.—Since the above was written, a paper by Markownikoff has appeared (*Annalen*, 1898, 302, 1) giving a detailed account of the preparation of derivatives of hexanaphthene from Caucasian naphtha, and his results, taken in conjunction with those in the present paper, conclusively show that the hydrocarbon,  $C_6H_{12}$ , boiling about  $80^\circ$  from Caucasian, from Galician, and from American petroleum is identical with synthetical hexamethylene.

UNIVERSITY COLLEGE,  
BRISTOL.

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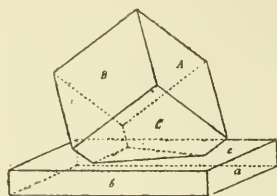
## XCVI.—*A Composite Sodium Chlorate Crystal in which the Twin Law is not Followed.*

By WILLIAM JACKSON POPE.

COMPOSITE crystals are either twins, in which rotation of the one crystalline individual about a common twin axis suffices to bring both into identical orientation, or else the crystalline individuals have intergrown in some chance position in which no symmetrical relation holds between the orientations of the individuals constituting the growth. The following case is of interest, as being apparently anomalous as regards the manner in which composition has occurred.

During the recent work of Kipping and Pope on enantiomorphism (*Trans.*, 1898, 606), several thousand sodium chlorate crystals were examined microscopically, and one crop of crystals, deposited from a pure aqueous solution, contained three presenting the appearance shown in the figure (next page); one of these three composite crystals was

removed from the solution in a fit state for measurement and was found not to have been formed in accordance with the ordinary twin law referred to above, but, nevertheless, the two individuals were orientated in a peculiarly symmetrical manner one to the other.



Each of the two crystals exhibit all the faces of the form  $\{100\}$ . The crystal forming the base of the combination is about a centimetre square and a millimetre thick, whilst the crystal standing upon the centimetre square base is almost a cube of 5—7 mm. edge. The measurements given below show that one four-fold axis of symmetry of the lower crystal coincides in direction with one three-fold axis of symmetry of the upper crystal. In the table, the capital letters refer to the faces on the cube-shaped crystal, the indices of which are enclosed in brackets; the calculations are made on the assumption that

Angle.	Measured values.	Calculated values.
$AB = (100) : (010)$	$89^{\circ}56'$	$90^{\circ}0'$
$BC = (010) : (001)$	$90\ 1$	$90\ 0$
$AC = (100) : (001)$	$90\ 5$	$90\ 0$
$bB = 010 : (010)$	$44\ 59$	$45\ 0$
$\bar{b}C = 0\bar{1}0 : (001)$	$45\ 3$	$45\ 0$
$aA = 100 : (100)$	$35\ 18$	$35\ 16$
$\bar{a}B = \bar{1}00 : (010)$	$65\ 51$	$65\ 54$
$\bar{a}C = \bar{1}00 : (001)$	$65\ 52$	$65\ 54$

the three-fold axis of symmetry of the one crystal coincides in direction with the four-fold symmetry axis of the other, and that the faces  $bBC\bar{b}$  are in a zone.

The close agreement between the observed and calculated angles on the composite crystal leads to the conclusion that the planes (111) and (011) on the cube-shaped crystal are respectively parallel to the planes (001) and (010) on the tabular crystal.

Both individuals are dextrorotatory and were firmly attached; on breaking them apart, an uneven surface was left at the plane of contact.

It would be interesting to know whether such cases of regularly orientated juxtaposition, in which the twin law is not followed, are common.

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## XCVII.—*Contributions to the Chemistry of Thoriums; Comparative Research on the Oxalates of the Rare Earth.\**

By BOHUSLAV BRAUNER, Ph.D., Professor of Chemistry in the Bohemian University, late Berkeley Fellow of Owens College.

### A. *Historical Introduction.*

IN continuing my researches on the chemistry of the "rare earth" metals (Trans., 1882, 41, 68; *Compt. rend.*, 1882, 94, 1718; *Monatsh.*, 1882, 3, 46; Trans., 1883, 43, 278; *ibid.*, 1885, 47, 879; *ibid.*, 1888, 53, 357; *Ber.*, 1891, 24, 1328; *Chem. News*, 1895, 71, 283) which were begun in 1878, attention has been directed to thorium.

Thorium, which belongs to the fourth group of the periodic system, is quadrivalent, whereas the other rare earth elements—notwithstanding cerium and praseodymium form compounds of a higher type than  $RX_3$ —are, in the majority of their compounds, trivalent. The author's attention was directed to the following reaction, by which thorium oxalate of the form  $RX_4$  is distinguished from the other oxalates of the form  $RX_3$ .

Bahr (*Annalen*, 1864, 132, 231) found, in 1864, that oxalate of "wasium" (which he found later on to be identical with thorium) is soluble in a warm solution of ammonium oxalate.

Bunsen (*Ann. Phys. Chem.*, 1875, 155, 375), in 1875, found that Bahr's reaction might be used for the preparation of pure thorium compounds; he observed that the oxalates of the cerium and yttrium earths, when boiled with an aqueous solution of ammonium oxalate and then largely diluted with water, remained in solution to a small extent only, whereas the solution of thorium oxalate in ammonium oxalate is not precipitated (decomposed) by the addition of water. It was, however, found necessary to repeat the process of conversion of this thorium-oxalate solution into the oxide, then into the sulphate, and again into the oxalate, dissolving the latter in

\* The principal results of the present research were communicated to the Toronto Meeting of the British Association on August 20, 1897.

ammonium oxalate, &c., many times, in order to get rid of the last traces of cerium and lanthanum, the presence of which was indicated by the spark spectra.

My intention was to study the interesting reaction of Bahr and Bunsen as fully as possible, in order to use it for the separation of thorium from the accompanying earth metals, and for the preparation of pure thorium compounds, as well as the determination of the atomic weight of thorium. But whereas, in Bunsen's experiments (and in those of his followers, who, however, did not throw any new light upon the problem in question), the thorium oxalate was dissolved by using an arbitrary quantity of ammonium oxalate, although undoubtedly in excess, I started on the supposition that the reaction in question is due to the formation of a definite double oxalate of thorium and ammonium, and my first task was to isolate this double salt, and to investigate its composition and properties. The second point was to establish, from the known composition and properties of this double salt, the minimum quantity of ammonium oxalate which would be sufficient to keep, say, 1 molecule of thorium oxalate in solution, and in this way to prevent the oxalates of the trivalent earth metals, which are undoubtedly far less soluble in ammonium oxalate, from being dissolved.

The object of the following research was to solve both these problems, namely, the preparation of the double salt, and the purification of the material based on the properties of this double salt.

### *B. Preparation of the Material.*

Thanks to the introduction of thorium compounds into the incandescent light industry by Dr. Auer, the material, which ten years ago was very scarce, has now become easily accessible, a large share of the credit for which is due to Dr. Shapleigh.

The following method was tried for the purification of thorium. Impure thorium nitrate was converted into the sulphate, and the latter treated with a saturated solution of sodium sulphate in such proportion that 4 parts of the double sulphate of sodium and thorium was contained in 100 parts of the solution; this method (and the subsequent recrystallisation of thorium sulphate from hot water, which was not used by me) was recommended some years ago by Cleve (*K. Svenska Vet. Akad. Handl.*, 2, No. 6, p. 187) for the purification of thorium, but although cerite metals were undoubtedly present, I found that not a trace of them was precipitated in the form of insoluble double sodium sulphates. From this solution, the thorium hydroxide was precipitated by ammonia, and, after being washed, was dissolved in hydrochloric acid and precipitated as oxalate; after washing and drying, this



oxalate was used for a preliminary atomic weight determination, which was made in a manner which will be fully described in a separate paper "On the Atomic Weight of Thorium."

The results obtained were:  $\text{ThO}_2 = 53.562$  per cent.  $\text{C}_2\text{O}_3 = 30.155$  per cent. At. weight of Th = 225.84.

This number is much lower than that found by Krüss and Nilson (*Ber.*, 1887, 20, 1675), Th = 232.45, and proves that cerite earths cannot be separated from thoria by means of sodium sulphate.

In order to prepare an approximately pure thorium oxalate, a strongly acid solution of the hydrochloride, prepared as described above, was heated to boiling, and a solution of oxalic acid added from a burette drop by drop with continuous stirring, until the heavy crystalline precipitate of thorium oxalate began to settle rapidly from the clear liquid. This oxalate was collected while hot, and washed with hot water containing about 1 per cent. of oxalic acid, in order to prevent its passing through the filter.

In this way, any zirconium present is removed, whereas if the oxalic acid solution be added in large quantity at once, zirconium will be carried down with the thorium oxalate, although alone it is not precipitated by oxalic acid under these conditions.

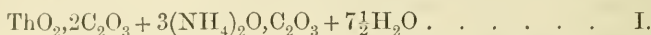
#### *C.—First Attempts to prepare the Double Salt.*

Part of the thorium oxalate, prepared as above described, was heated with water to boiling, and ammonium oxalate added in small portions at a time, until about half of the thorium oxalate had dissolved. When cold, the clear solution was filtered off from the insoluble portion consisting of the oxalates of thorium and the cerite earths, and the filtrate concentrated until, when allowed to cool, large, needle-shaped crystals began to form, consisting of ammonium oxalate contaminated only with a little thorium; the hot solution poured off from these slowly growing crystals now deposited smaller crystals of a different kind. On spontaneous evaporation, the solution solidified to a crystalline mass consisting of hexagonal plates belonging probably to the monoclinic system; it was, however, so thick and pasty that it was difficult to free the crystals from the mother liquor.

The air-dried crystals, as well as all the double oxalates of thorium and ammonium, were analysed in the following manner. The thorium was determined as dioxide,  $\text{ThO}_2$ , by heating the salt for a long time carefully, gradually raising the temperature, and heating at last strongly over the blast. In all cases, a double platinum crucible was used. The radicle of oxalic acid,  $\text{C}_2\text{O}_3$ , was determined with decinormal permanganate in a warm solution of 12.5 per cent. sulphuric acid in the manner to be described in the paper "On the Atomic

Weight of Thorium." Ammonium oxide was estimated by distillation with potash, &c., and water of crystallisation was determined from the loss at 105°. It was found convenient to express the composition of the salts and of the solutions analysed, in the old dualistic notation.

The analysis of the salt corresponds with the formula



	ThO <sub>2</sub> .	5C <sub>2</sub> O <sub>3</sub> .	3(NH <sub>4</sub> ) <sub>2</sub> O.	7½H <sub>2</sub> O.	Total.
Calculated * ... {	264.45	360.10	156.43	135.13	916.11
	28.87	39.30	17.08	14.75	100.00
Found .....	28.75	39.79	16.74	14.54	99.82

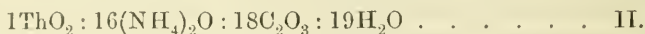
From the result of this analysis, it follows that, on using 3 mols. of ammonium oxalate for the dissolution of 1 mol. of thorium oxalate, a highly purified thorium salt, like the above, may be obtained at once, and at the same time hardly any appreciable quantity of cerite oxalates will dissolve.

In the following experiment, 13.64 grams of thorium oxalate, free from zirconia, corresponding with 11.42 grams of the anhydrous salt (= 1 mol.), were boiled with 11.94 grams (3 mols.) of ammonium oxalate in aqueous solution until no further diminution of the volume of the precipitate was observed; the clear solution was poured off from the insoluble colloidal residue which could not be separated by filtration, and which still contained a considerable quantity of thorium.

The *first* crop of crystals, obtained on evaporation of the solution, were long needles, and were analysed with the following result.

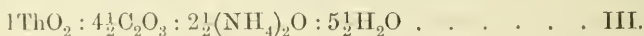
ThO<sub>2</sub> = 9.57 per cent.    C<sub>2</sub>O<sub>3</sub> = 47.68 per cent.    (NH<sub>4</sub>)<sub>2</sub>O = 30.13 per cent.  
H<sub>2</sub>O = 12.62 per cent.

From this follows the molecular relation:



We have here a mixture of the double salt with a large quantity of the relatively less soluble ammonium oxalate.

The *second* crop had the molecular composition,



	ThO <sub>2</sub> .	4½C <sub>2</sub> O <sub>3</sub> .	2½(NH <sub>4</sub> ) <sub>2</sub> O.	5½H <sub>2</sub> O.	Total.
Calculated . . . . .	264·45	324·09	130·39	99·09	818·02
	32·33	39·62	15·94	12·11	100·00
Found . . . . .	32·46	39·97	15·59 (16·09)†	11·48	99·50

\* The atomic numbers used in this paper are: O=16.00; H=1.008; C=12.01; N=14.04; Th=232.45.

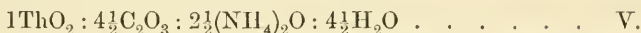
† The values, in brackets for ammonium oxide, are equal to the difference from 100, and they sometimes more nearly correspond with the truth than the direct determinations.

The molecular composition of the *third* crop was,



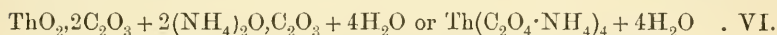
	ThO <sub>2</sub> .	4 $\frac{1}{3}$ C <sub>2</sub> O <sub>3</sub> .	2 $\frac{1}{3}$ (NH <sub>4</sub> ) <sub>2</sub> O.	4 $\frac{1}{3}$ H <sub>2</sub> O.	Total.
Calculated .....	264·45	312·09	121·70	78·07	776·31
	34·07	40·20	15·68	11·05	100·00
Found .....	33·91	40·47	15·57 (15·65)	9·97	99·92

The molecular composition of the *fourth* crop was,



	ThO <sub>2</sub> .	4 $\frac{1}{2}$ C <sub>2</sub> O <sub>3</sub> .	2 $\frac{1}{2}$ (NH <sub>4</sub> ) <sub>2</sub> O.	4 $\frac{1}{2}$ H <sub>2</sub> O.	Total.
Calculated .....	264·45	324·09	130·39	81·07	800·00
	33·06	40·51	16·30	10·13	100·00
Found .....	33·49	40·74	(15·53)	10·24	100·00

It is seen, on comparing the relations III, IV, and V, that the substances analysed consist of the double salt of thorium oxalate with ammonium oxalate, contaminated with a varying proportion of free oxalate of ammonium. Having regard to the circumstance that  $\text{Th}^{\text{IV}}\text{X}_4 + 4\text{RX} + 4\text{H}_2\text{O}$  is the most probable normal formula of a double salt of an element of the fourth group, we are entitled to subtract from the molecular relation obtained in III, IV, and V the small quantity of adhering ammonium oxalate, especially as it is only a small fraction of a molecule; thus after subtracting  $\frac{1}{2}$  or  $\frac{1}{3}[(\text{NH}_4)_2\text{C}_2\text{O}_4, \text{H}_2\text{O}]$  from the relations IV or V, the following most probable formula of the pure salt is obtained.



From the relations II and III, a salt with  $5\text{H}_2\text{O}$  is obtained, whereas on subtracting 1 mol. ammonium oxalate from I, we find that the salt crystallises with  $6\frac{1}{2}\text{H}_2\text{O}$ .

From these results, not only may the probable formula of the new double salt be inferred, but also that the salt crystallises with two different amounts of water.

#### D.—Solubility of the Double Salt.

The new double salt cannot be purified by recrystallisation from water, as it is hydrolytically decomposed by it into a white, colloidal precipitate, and ammonium oxalate; the decomposition is, however, only a partial one, as the ammonium oxalate, the soluble product of decomposition, keeps part of the double salt in solution. From this, it follows that the double salt cannot exist in aqueous solution without the simultaneous presence of free ammonium oxalate; it was impossible, therefore, to determine the solubility of the double salt in water

in the ordinary way, and so the only available method was to analyse a saturated solution of the nearly pure salt, that is, of the solution from which the nearly pure salt, III, began to crystallise out.

2.8235 grams of this mother liquor, on evaporation, and drying at  $105^{\circ}$ , gave a residue weighing 1.3340 grams, and the latter, on heating over the blast, left 0.4822 gram of  $\text{ThO}_2 = 17.29$  per cent. From these data, the composition is as follows.

$\text{Th}(\text{C}_2\text{O}_4)_2 = 26.71$  ;  $(\text{NH}_4)_2\text{C}_2\text{O}_4 = 20.54$  ;  $\text{H}_2\text{O} = 52.75$  per cent.

The molecular proportions of the constituents of the system are,

$1\text{Th}(\text{C}_2\text{O}_4)_2 : 2.53(\text{NH}_4)_2\text{C}_2\text{O}_4 : 45\text{H}_2\text{O}$  . . . . VII.

or  $\text{Th}(\text{C}_2\text{O}_4 \cdot \text{NH}_4)_4 + 0.53(\text{NH}_4)_2\text{C}_2\text{O}_4 + 45\text{H}_2\text{O}$ .

The solubility of the salt in water is expressed as follows. One hundred parts of water kept in solution 90.3 parts of the double salt,  $\text{Th}(\text{C}_2\text{O}_4 \cdot \text{NH}_4)_4 + 4\text{H}_2\text{O}$ , but 9.3 parts, or one additional half-molecular weight of ammonium oxalate, must be present in order to prevent the decomposition of the salt by water.

As thorium oxalate is practically insoluble in water, and as ammonium oxalate requires 4.5 parts of water for its solution,\* the mere circumstance that the new double salt is kept in solution by an equal quantity of water indicates that it is not a double salt in the ordinary sense of the word, but a *complex* compound, namely, the ammonium salt of thoroxalic acid or *ammonium thoroxalate*.

#### E.—*New Experiments to Prepare the Complex Salt.*

Thoroxalate of ammonium exhibits in a high degree the tendency to form supersaturated solutions—a circumstance which will be treated more fully below—and this property was used in order to prepare the new salt in a pure state.

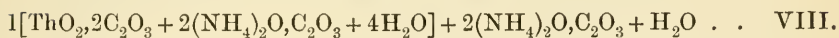
64.8 grams of ordinary thorium oxalate (1 mol.) containing 54.44 per cent. of  $\text{ThO}_2$  was mixed with 46.5 grams of crystallised ammonium oxalate ( $2\frac{1}{2}$  mols.) and boiled with 100 c.c. of water; a considerable portion of thorium oxalate remained undissolved. The turbid liquid was then considerably diluted with water in order to secure the precipitation of the oxalates of the other rare earths, and when the solution became clear, half of the liquid was syphoned off, and carefully evaporated to the original concentration, so that, on cooling, the greatest

\* 10.175 grams (= 10 c.c.) of a solution of ammonium oxalate saturated at  $17^{\circ}$ , in contact with undissolved, solid salt, contained, according to a volumetric determination with permanganate, 0.44107 gram of the crystallised salt, therefore, 1 part is soluble in 4.531 parts of water or 22.07 parts in 100 parts of water.

part of the salt crystallised out. The analysis of the first crop of crystals gave the following result.

$\text{ThO}_2 = 25.66$  ;  $\text{C}_2\text{O}_3 = 42.59$  ;  $\text{H}_2\text{O} = 11.43$  ;  $(\text{NH}_4)_2\text{O} = 20.32$  per cent.

The composition of the crystals is therefore,



The crystals contain far less free ammonium oxalate than the first crystallisation, II, of the former series.

After some time, the dense mother liquor, the volume of which was about 20—30 c.c., was poured off carefully from the crystals into a small beaker, when immediately, before the eyes of the observer, beautiful, glistening, well-formed crystals several mm. in length began to grow downwards from the surface of the highly supersaturated liquid. After some time, when the growth of the crystals had ceased, the solution was poured off into another small beaker; owing to a new impulse, a fresh growth of large crystals took place from the solution which was still supersaturated, although it contained the same crystals as "ground substance"; moreover, the operation of pouring off the solution and the immediate formation of fresh crystals could be repeated four times within a few hours. In this way, crops of crystals Nos. 2, 3, 4, and 5 were obtained, and it was only when the mother liquor was poured off from No. 5 that the property of crystallising so rapidly and the strong supersaturation ceased.

The crystals obtained in the four crystallisations Nos. 2, 3, 4, and 5 were separately dried by pressing between smooth filter paper, and after being kept only a short time in well closed vessels, they were analysed with especial care, with the following results.

No. 2. 0.7474 gram of the salt, when dried at  $107^\circ$ , lost 0.1202 gram = 16.08 per cent., and at  $127^\circ$ , 0.1204 gram = 16.11 per cent.  $\text{H}_2\text{O}$ , and after heating more strongly, at last over a blowpipe, 0.2527 gram  $\text{ThO}_2 = 33.81$  per cent. was left.

0.6001 gram, on titration with permanganate, gave 0.2214 gram  $\text{C}_2\text{O}_3 = 36.89$  per cent.

0.7066 gram gave 0.09464 gram  $(\text{NH}_4)_2\text{O} = 13.39$  per cent.

No. 3. 0.97905 gram, when kept over phosphorus pentoxide for 9 days at  $20^\circ$ , lost 0.1547 gram = 15.80 per cent.; after drying at  $105^\circ$ , 0.1552 gram = 15.85 per cent., and at  $125$ — $130^\circ$ , 0.15625 gram = 15.96 per cent.  $\text{H}_2\text{O}$ .

After heating over the blowpipe, a residue of 0.3309 gram = 33.798 per cent.  $\text{ThO}_2$  was obtained.

0.5445 gram gave 0.20208 gram  $\text{C}_2\text{O}_3 = 37.11$  per cent.

No. 4. 1.2701 gram salt, at  $105^\circ$ , lost 0.20375 gram = 16.04 per cent.  $\text{H}_2\text{O}$ , leaving a residue of 0.4829 gram = 33.77 per cent.  $\text{ThO}_2$ .



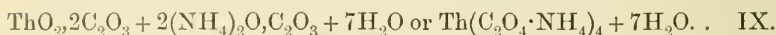
0.40095 gave 0.1479  $C_2O_3$  and 0.5481 gave 0.20208  $C_2O_3$  = 36.887 and 36.87 per cent.

0.6199 gram gave 0.08286  $(NH_4)_2O$  = 13.37 per cent.

No. 5. 1.2147 gram, at  $107^\circ$ , lost 0.1952 gram = 16.07 per cent., and at  $125-130^\circ$ , 0.1964 gram = 16.17 per cent.  $H_2O$ , leaving a residue of 0.4047 gram = 33.32 per cent.  $ThO_2$ .

0.5971 gram gave 0.22185 gram  $C_2O_3$  = 37.15 per cent.

All these data correspond exactly to the formula,



Calculated.		Found.			
		No. 2.	No. 3.	No. 4.	No. 5.
$ThO_2$ = 264.45	33.78	33.81	33.80	33.77	33.32
$4C_2O_3$ = 288.08	36.79	36.89	37.11	36.88	37.15
$2(NH_4)_2O$ = 104.29	13.32	13.39	(13.13)	13.37	(13.36)
$7H_2O$ = 126.11	16.11	16.11	15.96	16.04	16.17
782.93	100.00	100.20	100.00	100.06	100.00

Fraction No. 5 evidently already contained a slight admixture of free ammonium oxalate. The fractions Nos. 2, 3, and 4 were almost absolutely pure, and gave as a mean 33.789 per cent. of thorium dioxide. From the ratio  $33.789 : 66.211 = x : 518.48$  (that is,  $4C_2O_3 + 2(NH_4)_2O + 7H_2O$ ), the molecular weight  $ThO_2 = 264.59$  is calculated from which follows  $Th = 232.59$  as the atomic weight of thorium.

#### F.—*Properties of Ammonium Thoroxalate.*

It follows from the comparison of the formulæ given in VI and IX that the complex salt investigated occurs in the form of two hydrates: the one form, which crystallised on spontaneous evaporation of the solution, contains  $4H_2O$ , whereas the second, which has hitherto been obtained only by inducing the crystallisation of a supersaturated solution, contains  $7H_2O$ . This circumstance may be regarded as a new confirmation of the rule established by Potilizin, that "compounds forming supersaturated aqueous solutions appear in more than one hydrated form."

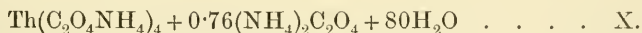
The above supersaturated solution seems to be, in the first place, "supersaturated," with regard to the hydrate with  $4H_2O$ , for the crystallisation from this solution does not take place even when the tetrahydrated salt exists in it for several days as a sedimentary or "ground substance." It appears, however, that the solution may also exist in a state of supersaturation with regard to the hydrate with  $7H_2O$ , for a mechanical impulse is always necessary in order to induce the crystallisation of *one part* of the heptahydrate, and this unstable equilibrium

is only partly destroyed by the growth of the crystals, which after a time ceases, so that only by new mechanical impulses can new quantities of the salt be induced to crystallise.

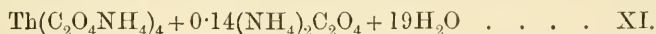
It has hitherto been impossible to study these phenomena from the physico-chemical point of view, for as the salt undergoes hydrolytic decomposition in contact with water, it can only exist in aqueous solution in the presence of one of the products of its decomposition, ammonium oxalate, and this hydrolytic decomposition is a very complex process, as will be seen in the following sections.

Another circumstance should be pointed out. From VI, as well as from the experiments on the decomposition of ammonium thoroxalate by water described further down, it follows that the minimum quantity of ammonium oxalate necessary to keep the ammonium thoroxalate from undergoing decomposition in a saturated concentrated solution of the salt is a half-molecule. This gives rise to the question: What quantity of free ammonium oxalate was contained in the "*supersaturated*" solution from which a perfectly pure ammonium thoroxalate free from mechanically adhering ammonium oxalate was obtained?

The calculation may be made from the following data. The sum of the weights of the pure crystallisations Nos. 2, 3, 4, and 5 was 26.18 grams, the last mother liquor contained, in 100 parts,  $\text{ThO}_2 = 12.09$ ,  $\text{C}_2\text{O}_3 = 15.68$ ,  $(\text{NH}_4)_2\text{O} = 6.60$ , and  $\text{H}_2\text{O} = 65.63$ . Its molecular composition was therefore,



As 100 parts of this solution contained 12.09  $\text{ThO}_2$ , but 100 parts of the solid residue left by this solution on evaporation contained 29.60  $\text{ThO}_2$  and 38.46  $\text{C}_2\text{O}_3$ , the 4.203 grams of the residue obtained corresponded with 10.287 grams of the solution, its total weight being 14.122 grams. Therefore, 100 parts of the *original* solution, before the separation of the crop of crystals No. 2, contained:  $\text{ThO}_2 = 26.11$ ,  $\text{C}_2\text{O}_3 = 29.54$ ,  $(\text{NH}_4)_2\text{O} = 10.91$ , and  $\text{H}_2\text{O} = 33.44$ . From this it is calculated that the molecular composition of the original *supersaturated* solution was,



In this solution, two parts of the anhydrous ammonium thoroxalate are kept dissolved by one part of water.

The beautifully formed crystals of the heptahydrated ammonium thoroxalate have a strong lustre, but their surface soon became dull on exposure to the air, even in closed vessels. The crystals were therefore unsuitable for crystallographic examination.

The hydrate with  $7\text{H}_2\text{O}$  is the more labile one, and it is completely converted, even in air of ordinary humidity, into the more stable hydrate with  $4\text{H}_2\text{O}$ , as seen from the following experiment.

0.7185 gram of the finely powdered salt was exposed to air of ordinary humidity, but so that dust had no access to it, and weighed frequently. After 23 days, the loss of weight amounted to 0.0490 gram = 6.82 per cent., after 50 days to 0.05 gram = 6.96 per cent., whereas the calculated loss for  $3\text{H}_2\text{O}$  is 6.90 per cent., and no further loss took place after the lapse of 13 months.

Another loss of water takes place in a dry atmosphere, for, as seen from the analysis of No. 3, the loss of weight over phosphorus pentoxide after 9 days amounted to 15.80 per cent., or the salt loses almost the whole of its water of crystallisation, the quantity calculated for  $7\text{H}_2\text{O}$  being 16.11 per cent. After exposure to ordinary air for 9 days, only 1.48 per cent. of water was taken up again.

This behaviour is in accordance with the fact that we have to deal with a complex salt and not with a double salt of the ordinary kind, for its constituents behave in a different manner. Ammonium oxalate loses its water of crystallisation only at  $100^\circ$ , whereas thorium oxalate retains  $2\text{H}_2\text{O}$  even after drying at  $100^\circ$ . Moreover, ammonium oxalate loses part of its ammonia at  $100^\circ$ , becoming acid, but ammonium thoroxalate may be dried at  $127^\circ$  without losing any ammonia, and it is only at  $150^\circ$  that a partial decomposition takes place, as seen from the following experiment.

0.6270 gram of the anhydrous salt, after heating for 6 hours at  $150^\circ$ , lost 0.0070 gram = 1.12 per cent., and after 6 hours more, at  $190^\circ$ , it lost 0.0188 gram more = 3.00 per cent.

On heating to a higher temperature, the salt is decomposed, and large quantities of cyanogen, easily recognisable by its odour, are evolved; at the same time, paracyanogen is formed. It is known that Dumas found cyanogen among the products of the decomposition of ammonium oxalate by heat, but comparative experiments I have made show that the smell of cyanogen evolved on heating ammonium oxalate (which loses much ammonia above  $100^\circ$ ) is far less pronounced than that obtained with a corresponding quantity of ammonium thoroxalate.

#### *G.—Hydrolytic Decomposition of Ammonium Thoroxalate.*

When solid ammonium thoroxalate is brought into contact with water, hydrolytic decomposition takes place, a white precipitate is formed, and the solution contains thorium and ammonium in the form of oxalates, that is, a certain quantity of dissolved ammonium thor-

oxalate, together with an excess of free ammonium oxalate. The quantity of the salt decomposed and that of the insoluble and of the soluble products of decomposition is a function of the amount of water used for the decomposition.

It is known that thorium oxalate is soluble in an aqueous solution of ammonium oxalate, and so at first sight it seemed probable that the white precipitate formed in the above process of decomposition consisted of thorium oxalate, the compounds (*a*) ammonium thoroxalate and (*b*) thorium oxalate, ammonium oxalate, and water being the *two* sides or phases of an ordinary reversible reaction. It was my intention to investigate whether the white insoluble compound was ordinary thorium oxalate or not. Unfortunately, however, this precipitate is a colloidal substance, which, when attempts are made to collect it by filtration, passes entirely through the filter, and if after repeated filtration some of it may remain on the filter, washing with water produces a milky liquid which again passes through the filter, so that it was impossible to isolate the precipitate for analysis. Yet in connection with the experience gained at a much later period of the present research, as described in Section L entitled "A new thoroxalate of thorium and ammonium" (p. 980), it was possible to determine the composition of this colloidal precipitate by an indirect method.

*Exp.* 1. 2.1374 grams of the pure thoroxalate of ammonium,  $\text{Th}(\text{C}_2\text{O}_4 \cdot \text{NH}_4)_4 + 7\text{H}_2\text{O}$ , the analysis of which was described in section E, was placed in a measuring flask of 25 c.c., and 6 c.c. of water of  $24^\circ$  was poured over it; on shaking, the temperature fell to  $19^\circ$ , the solution and decomposition by water being an endothermic process. After this, 18 c.c. more water was added, so that the total quantity of water was 23.991 grams, the flask being repeatedly shaken until a homogeneous, milky liquid was obtained; this required a long time to become quite clear, so that it was not until after two months standing that weighed portions of the clear liquid could be analysed.

5.1296 grams of the liquid (sp. gr. = 1.026) was weighed in a crucible, which was placed in a closed weighing flask (a similar vessel containing platinum served as a tare), the liquid was evaporated on the water bath, and the residue heated gradually until the oxalic acid and ammonia were destroyed, finally over the blast, so that only thorium dioxide was left. This weighed 0.07 gram, so that 100 parts of the liquid contained 1.3647 parts of  $\text{ThO}_2$ .

In another portion, weighing 5.1151 grams, the oxalic acid radicle,  $\text{C}_2\text{O}_3$ , was determined, by means of permanganate, after acidifying with dilute sulphuric acid, when 0.10633 gram of  $\text{C}_2\text{O}_3$  was found = 2.07865 per cent.  $\text{C}_2\text{O}_3$ . As thorium and ammonium were present in the form of normal salts, it was unnecessary to make a determination of



ammonia, as the quantity of ammonium oxide present could be determined by calculation.

The 1.3647 per cent. of  $\text{ThO}_2$  require 0.74328 per cent.  $\text{C}_2\text{O}_3$  in order to form 2.10798 per cent. of the normal anhydrous thorium oxalate, so that the remaining 1.33537 per cent. of  $\text{C}_2\text{O}_3$  forms, with 0.96682 per cent. of  $(\text{NH}_4)_2\text{O}$ , 2.30219 per cent. of anhydrous ammonium oxalate. The total of the solids in solution is therefore 4.41017 per cent., and the difference from 100 = 95.5898 is the percentage of water in the solution.

Now the 2.1374 grams of the salt  $\text{Th}(\text{C}_2\text{O}_4 \cdot \text{NH}_4)_4 + 7\text{H}_2\text{O}$  used contain 0.67794 gram of  $(\text{NH}_4)_2\text{C}_2\text{O}_4 (=o)$ , and 1.11518 grams of  $\text{Th}(\text{C}_2\text{O}_4)_2 (=o_1)$ , and 0.34428 gram of water, which, together with the 23.911 grams of water used for the decomposition of the salt, gives a total of 24.3353 grams of water present in the flask.

As the object was to calculate the *composition* as well as the *quantity* of the precipitate, it was convenient, in obtaining a *first* approximation, to assume that the precipitated solid contained no water.

*a.*—From the above data, first the absolute quantity of ammonium oxalate contained in the solution was calculated as follows: ( $\text{H}_2\text{O}$  in the solution = 95.5898 per cent.,  $(\text{NH}_4)_2\text{O}$  in the solution = 2.30219 per cent., and the absolute quantity of water = 24.3353 grams)  $95.5898 : 2.30219 = 24.3353 : x$ , from which  $x = 0.58612$  gram. The difference between this number and the total quantity of ammonium oxalate  $o$  present ( $o - x$ , or  $0.67794 - 0.58612$ ) = 0.09182 gram, which is the quantity of ammonium oxalate contained in the precipitate.

*b.*—In the same way, the absolute quantity of thorium oxalate contained in the solution is calculated [ $\text{Th}(\text{C}_2\text{O}_4)_2$  in the solution = 2.10798 per cent., the two values for water are the same as in *a*],  $95.5898 : 2.10798 = 24.3353 : y$ , from which  $y = 0.53666$  gram. The difference between this number and the total quantity of thorium oxalate  $o_1$  present ( $o_1 - y$ , or  $1.11518 - 0.53666$ ) = 0.57852 gram, which is the quantity of thorium oxalate contained in the precipitate. Now, on dividing the quantities of ammonium oxalate and of thorium oxalate contained in the precipitate, as calculated from *a* and *b*, by the molecular weights of these oxalates, the following molecular ratio is obtained:  $\text{Th}(\text{C}_2\text{O}_4)_2 : (\text{NH}_4)_2\text{C}_2\text{O}_4 = 1 : 0.522$ , which shows that the white, colloidal precipitate does not consist of ordinary thorium oxalate, but that it contains half a molecule of ammonium oxalate, combined, for every molecule of thorium oxalate.

It will be seen from Section I. (p. 980) that, at a much later period of the present research, a compound was obtained which was also colloidal at first, but became crystalline after the lapse of several months. The composition of these crystals is expressed by the formula

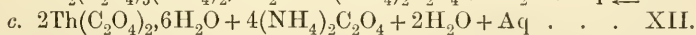
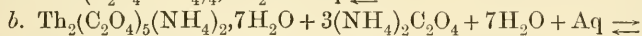
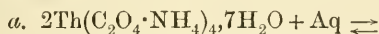


$2\text{Th}(\text{C}_2\text{O}_4)_2 \cdot (\text{NH}_4)_2\text{C}_2\text{O}_4 + 7\text{H}_2\text{O}$ , or it is a "quarter-saturated" thoroxalate of ammonium. As this compound was obtained by hydrolytic decomposition of the normal thoroxalate of ammonium which was originally completely dissolved in water, there can be no doubt that our colloidal precipitate is only a colloidal modification of this compound, and it may be assumed that it also contains  $7\text{H}_2\text{O}$ .

The sum of the quantities of the oxalates of ammonium and thorium calculated in *a* and *b*, namely,  $0.09182 + 0.57582 = 0.67034$  gram, represents the quantity of the colloidal compound regarded as anhydrous, and, as in the heptahydrated salt, for every 88.18 parts of the anhydrous salt, 11.82 parts of water are contained (see analysis in Section I), it follows that the colloidal substance contains 0.08985 grams of water, so that its total weight is 0.76019 gram.

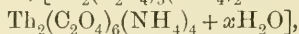
This quantity of water must be subtracted from the total quantity of water present in the solution  $24.3353 - 0.08985 = 24.2455$  grams, and this number must be substituted for the value  $\text{H}_2\text{O} = 24.3353$  grams in the equations *a* and *b*. This *second* calculation gives  $x = 0.58394$  grams and  $o - x = 0.094$ , and equally  $y = 0.53467$  and  $o_1 - y = 0.58051$  grams. The molecular ratio,  $\text{Th}(\text{C}_2\text{O}_4)_2 : (\text{NH}_4)_2\text{C}_2\text{O}_4 = 1 : 0.533$ ,  $\text{H}_2\text{O}$  in the precipitate  $= 0.09042$  gram, weight of the precipitate  $= 0.76492$  gram. A *third* calculation with this last value for water gives a result which may be regarded as final, for it does not differ sensibly from that obtained in the second calculation. We obtain  $x = 0.58393$  gram and  $o - x = 0.094$  gram,  $y = 0.53466$  gram and  $o_1 - y = 0.58052$  gram. The molecular ratio is  $1 : 0.533$ , and  $\text{H}_2\text{O}$  in the precipitate  $= 0.09042$  gram, so that the total weight of the precipitate is  $= 0.76495$  gram. It is seen that the repeated calculations do not alter the molecular ratio between the oxalates of thorium and ammonium in the precipitate.

The results of the experiment, described at some length, lead to the interesting conclusion that the action of water on ammonium thoroxalate, as well as the action of ammonium oxalate on thorium oxalate in aqueous solution, is a reversible process, having *three phases* (not "phases" in Gibbs' sense).



The above experiment enables us to calculate the real amount of the solid product of decomposition yielded by a definite quantity of solid ammonium thoroxalate, and of the quantity of the latter existing in the aqueous solution in the presence of a definite quantity of ammonium oxalate. Of course, thoroxalate of ammonium does not exist as such in what we call its aqueous solution, being partly hydro-

lysed and partly ionised, but it was impossible to include questions of this kind in the present research, which is already too extended, having required several years of work, incomplete as it is. For the treatment of the decomposition of ammonium thoroxalate by water from the point of view of Gibbs' phase rule is a very complicated problem, as not only the oxalates of thorium and of ammonium appear as products of decomposition, but certainly one and probably two intermediate compounds,  $[\text{Th}_2(\text{C}_2\text{O}_4)_5(\text{NH}_4)_2 + 7\text{H}_2\text{O}]$  and



are formed.

The ratio between the final values for the quantity of thorium oxalate  $y$  contained in the aqueous solution, and between that contained in the precipitate  $(o_1 - y)$  is  $\frac{y}{o_1 - y} = \frac{0.53466}{0.58052} = \frac{1}{1.086}$ , this number re-

presenting their molecular ratio. The ratio between the quantity of thorium oxalate contained in the aqueous solution  $y$ , and between the quantity of ammonium oxalate  $x$  contained in the same solution is

$x/y = \frac{0.58393}{0.53466}$ , and on dividing these two numbers by the correspond-

ing molecular weights, the following ratio is obtained for the substances existing in aqueous solution,  $\text{Th}(\text{C}_2\text{O}_4)_2 : (\text{NH}_4)_2\text{C}_2\text{O}_4 = 1 : 3.593$ . The sum of the molecular quantities of thorium oxalate contained in the solution ( $=1$  mol.), and that contained in the precipitate ( $=1.086$ )  $=2.086$  being taken as the starting point, the decomposition of this molecular quantity of ammonium thoroxalate by water is expressed as follows.

$2.086[\text{Th}(\text{C}_2\text{O}_4 \cdot \text{NH}_4)_4, 7\text{H}_2\text{O} + 488\text{Aq}]$  gives,

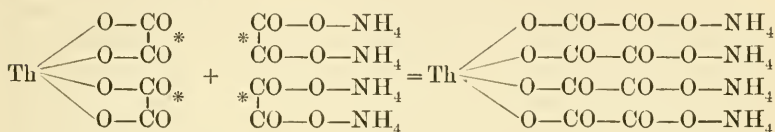
Dissolved :  $\text{Th}(\text{C}_2\text{O}_4 \cdot \text{NH}_4)_4 + 1.59(\text{NH}_4)_2\text{C}_2\text{O}_4 + 1028\text{Aq}$ , and

Insoluble :  $0.543[\text{Th}_2(\text{C}_2\text{O}_4)_5(\text{NH}_4)_2 + 7\text{H}_2\text{O}]$  . . . XIII.

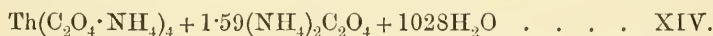
In performing the following experiments, practical purposes were kept in view as the first object. In order to prepare a thorium compound free from other rare earths, it was necessary to ascertain : What is the smallest molecular quantity of ammonium oxalate necessary for dissolving a molecular quantity of thorium oxalate and keeping it dissolved in an aqueous solution of varying concentration ?

For this purpose, either, *a*, ammonium thoroxalate was decomposed by water, or, *b*, thorium oxalate was treated with ammonium oxalate and water ; in the latter case, it was found that thorium oxalate is only slowly dissolved in a dilute solution of ammonium oxalate even at  $100^\circ$ , whereas when, in accordance with the ratio, VI, for 100 parts of water 45 parts of ammonium oxalate were used, large quantities of thorium oxalate were found to pass easily and quickly into the solution

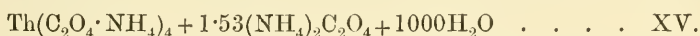
at 100°. This seems to be explained by the circumstance that the formation of the complex salt is not a mere additive process, but that it is preceded by the splitting up of the valencies between the CO-groups, in which case a resistance has to be overcome.



From Exp. 1, it follows that the aqueous solution of ammonium thoroxalate contains the following molecular quantities.

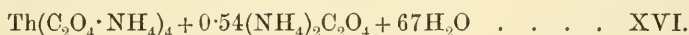


Exp. 2. The portion remaining from Exp. 1 was boiled, but the solution was analysed only after it was cold and had become clear; 100 parts of the solution contained 1.403 parts  $\text{ThO}_2$  and 2.111 parts  $\text{C}_2\text{O}_3$ , or  $\text{Th}(\text{C}_2\text{O}_4)_2 = 2.166$  parts,  $(\text{NH}_4)_2\text{C}_2\text{O}_4 = 2.322$  parts, and  $\text{H}_2\text{O} = 95.511$  parts. The solution contained the following molecular quantities.



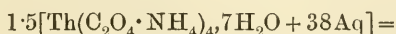
Exp. 3. 5.8393 grams of the pure ammonium thoroxalate was treated in a closed cylinder with 5.84 grams of water. A considerable diminution of temperature occurred, and as the complete decomposition proceeded only very slowly in the pasty mixture, the closed cylinder was heated to 100°, and its contents repeatedly shaken. A milky emulsion was formed, which took a long time to clear. The small volume of the clear solution standing above the white colloidal precipitate was, after 9 months standing, removed by a pipette and analysed.

One hundred parts of the solution contained 13.69 parts  $\text{ThO}_2$  and 16.918 parts  $\text{C}_2\text{O}_3$ , or  $\text{Th}(\text{C}_2\text{O}_4)_2 = 21.146$  parts  $(\text{NH}_4)_2\text{C}_2\text{O}_4 = 16.312$  parts, and  $\text{H}_2\text{O} = 65.542$  parts. In this solution, the following molecular quantities were contained.



This is the most concentrated saturated solution which can exist at the ordinary temperature.

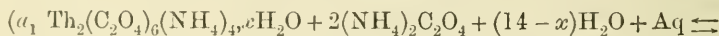
On calculating the composition of the solution and of the precipitate, and the quantity of the latter, in the same way as described in Exp. 1, the following approximate molecular representation of the hydrolytic decomposition of the salt is obtained.



Dissolved:  $\text{Th}(\text{C}_2\text{O}_4 \cdot \text{NH}_4)_4 + 0.54(\text{NH}_4)_2\text{C}_2\text{O}_4 + 67\text{H}_2\text{O}$ , and

Insoluble:  $0.5[\text{Th}(\text{C}_2\text{O}_4)_2 + (\text{NH}_4)_2\text{C}_2\text{O}_4] \quad . \quad . \quad . \quad \text{XVII.}$

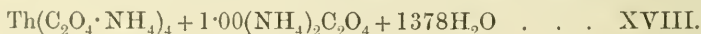
The precipitate contains an equal number of molecules of thorium oxalate and ammonium oxalate, and consists either of a new "half-saturated" ammonium thoroxalate, intermediate between the normal salt and the "quarter-saturated" salt, or of a mixture of an equal number of molecules of the latter and of the unaltered normal compound. If the first view is correct, which is not improbable, this compound must be regarded as the first product of hydrolytic decomposition of ammonium thoroxalate and as the ammonium derivative of acid thorium oxalate,  $\text{Th}_2(\text{C}_2\text{O}_4)_6\text{H}_4$ , and a new *fourth* phase between *a* and *b* would be added to the reversible process of hydrolytic decomposition represented in XII.



*Exp. 4.* 1.66 grams of the complex salt was boiled with 1.66 grams of water, and crystals of ammonium oxalate were added; the solution became clear after the addition of 0.1 gram of ammonium oxalate. It was diluted with water to 50 c.c., and after being kept 3 days, spherical aggregates of crystals were found on the bottom of the flask. The clear liquid was analysed, with the following result.

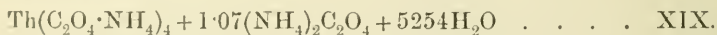
One hundred parts of the solution contained 1.0349 parts  $\text{ThO}_2$  and 1.4115 parts  $\text{C}_2\text{O}_3$ , or  $\text{Th}(\text{C}_2\text{O}_4)_2 = 1.5986$  parts  $(\text{NH}_4)_2\text{C}_2\text{O}_4 = 1.4616$  parts, and  $\text{H}_2\text{O} = 97.1398$  parts.

The solution contained the following molecular quantities.



*Exp. 5.* The portion of solution remaining from *Exp. 4* was diluted with much water, and the clear solution was analysed after 9 days standing.

100 parts of the solution contained:  $\text{ThO}_2 = 0.27704$  part and  $\text{C}_2\text{O}_3 = 0.38273$  part or  $\text{Th}(\text{C}_2\text{O}_4)_2 = 0.4279$  part,  $(\text{NH}_4)_2\text{C}_2\text{O}_4 = 0.3997$  part and  $\text{H}_2\text{O} = 99.1724$  parts. The solution contained the following molecular quantities.



From this solution, after a considerable time, a further separation of a crystalline solid took place.

The experiments No. 4 and No. 5, but *not* Nos. 1 and 2, permit the following conclusion to be drawn.

If thorium oxalate is pure, *one* molecular quantity of this salt, when treated with *three* molecular quantities of ammonium oxalate and water, give a solution which remains clear for some time, even after dilution with a considerable quantity of water.

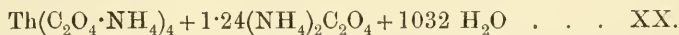


The following experiments were made in order to test the truth of this thesis.

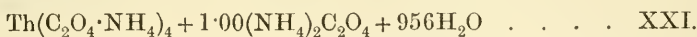
*Exp. 6.* 2.1372 grams of pure thorium oxalate, prepared from the pure complex salt, and containing 51.908 per cent. or 1.1094 gram of  $\text{ThO}_2$  (1 mol), was mixed with 1.7893 grams or 3 molecular proportions of ammonium oxalate, and to 4.0265 grams of this mixture 8 grams of water was added. After raising the temperature of the whole to  $100^\circ$ , an immediate and complete solution took place, and the liquid, on adding 38 parts of water for each part of ammonium oxalate, remained clear for some time.

*Exp. 7.* 1.4590 grams of pure thorium oxalate containing 0.7750 gram of  $\text{ThO}_2$  (1 mol.) was mixed with 1.25 gram (3 mols.) of ammonium oxalate, and 6 c.c. of water was added; at  $100^\circ$ , a clear solution was obtained at once. The solution was diluted with water to 50 c.c. and remained clear for 5 days in a closed vessel; on the sixth day, however, a slight turbidity appeared, and later on a white precipitate separated from the liquid. After several weeks, this precipitate became crystalline, and adhered to the glass walls of the vessel. The perfectly clear solution was analysed after a lapse of 6 months.

One hundred parts of the solution contained 1.3638 parts  $\text{ThO}_2$  and 1.9450 parts  $\text{C}_2\text{O}_3$  or  $\text{Th}(\text{C}_2\text{O}_4)_2 = 2.106$  parts,  $(\text{NH}_4)_2\text{C}_2\text{O}_4 = 2.073$  parts, and  $\text{H}_2\text{O} = 95.821$  parts. The solution contained the following molecular quantities.



Originally, before the separation of the crystalline precipitate, the ratio was,



The difference between the composition of the solution in the two cases is due to the fact that part of the thorium originally contained in the solution was separated after 6 months standing in the form of the solid "quarter-saturated" ammonium thoroxalate,  $\text{Th}_2(\text{C}_2\text{O}_4)_5(\text{NH}_4)_2 + 7\text{H}_2\text{O}$ .

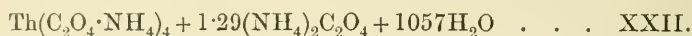
*Exp. 8.* 29.324 grams of the purest thorium oxalate, prepared from the pure complex salt and once more purified by crystallisation from nitric acid (see Section M), and containing 15.221 grams of  $\text{ThO}_2$  (1 mol.) was mixed with 24.55 grams (or 3 mols.) of ammonium oxalate and 50 c.c. of water; on applying heat to this mixture, a clear solution was obtained easily and rapidly; this was further diluted with 850 c.c. of water (total water = 900 c.c.). After some time, a turbidity was produced and became considerable after 5 days; later on, this colloidal precipitate first formed was converted into a crystalline substance, of which a considerable quantity was found on the bottom and on the walls of the vessel.



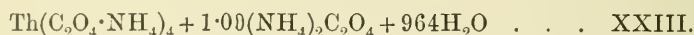
After 5 months standing, one part of the clear solution was used for analysis, whilst the principal portion of the solution was left in the closed vessel in contact with the precipitate, which was collected and analysed after another lapse of 10 months (see Section L, p. 980).

One hundred parts of the solution contained  $\text{ThO}_2 = 1.3328$  and  $1.3312$  parts (mean  $= 1.332$  parts), and  $\text{C}_2\text{O}_3 = 1.9180$  and  $1.9182$  parts (mean  $= 1.918$  parts), or  $\text{Th}(\text{C}_2\text{O}_4)_2 = 2.0575$  parts,  $(\text{NH}_4)_2\text{C}_2\text{O}_4 = 2.057$  parts and  $\text{H}_2\text{O} = 95.8855$  parts.

The solution contained the following molecular quantities.



Originally, before the separation of the crystalline precipitate, the ratio was



In this case also, a part of the thorium oxalate originally contained in the solution was separated in the form of solid "quarter-saturated" ammonium thoroxalate (already mentioned in Exp. I, and analysed in Section L), and it may be said that the solution was originally "supersaturated" with regard to this compound, this unstable equilibrium being destroyed only after a considerable length of time.

The results of the experiments may be seen from the following comparative arrangement; Col. II contains the molecular quantities of ammonium oxalate which are necessary in order to keep, in presence of the molecular quantities of water given in Col. III, one molecule of ammonium thoroxalate in solution. This is represented in Col. I, where the Roman numbers refer to the molecular ratios calculated from the analytical results.

I.		II.	III.
$\text{Th}(\text{C}_2\text{O}_4 \cdot \text{NH}_4)_4$ .		$(\text{NH}_4)_2\text{C}_2\text{O}_4$ .	$\text{H}_2\text{O}$ .
Ratio.	Mol.	Mols.	Mols.
IX	1	0.00	7 (solid salt)
XI	1	0.14	19
VII	1	0.53	45
XVI	1	0.54	67
X	1	0.76	80
XXI	1	1.00	956
XXIII	1	1.00	964
XVIII	1	1.00	1378
XIX	1	1.07	5254
XX	1	1.24	1032
XXII	1	1.29	1057
XV	1	1.53	1000
XIV	1	1.59	1028

The numbers of Col. II are *not* proportional to the dilution, Col. III, for the following reasons.

The solution in XI was supersaturated with regard to the salt  $\text{Th}(\text{C}_2\text{O}_4 \cdot \text{NH}_4)_4 + 7\text{H}_2\text{O}$ ; the solution in VII appears abnormal for some unknown reason; the solution in XVI was the most concentrated saturated one. The solutions in XXI, XXIII, XVIII, and XIX have not yet reached a state of equilibrium, being supersaturated with regard to the salt  $\text{Th}_2(\text{C}_2\text{O}_4)_5(\text{NH}_4)_2 + 7\text{H}_2\text{O}$ . The circumstance that the numbers in XX and XXII, that is, 1.24 and 1.29, are not identical with the numbers 1.53 and 1.59 obtained in XV and XIV at the same dilution, proves that it is not the same whether a supersaturated solution of the salt, or whether the solid salt itself, is decomposed by water. Probably also, in the last cases, the equilibrium was not yet reached, that is, during the decomposition of the solid salt by water—owing to the impossibility of a complete action of *all* the water on the *whole* of the salt—a little more free ammonium oxalate was formed in solution, which at this high dilution was unable to dissolve the small quantity of thorium oxalate still required. For the same reason, the factor for ammonium oxalate, 1.53, was smaller when the water acted at  $100^\circ$ , than the factor 1.59, which was obtained when the action of water proceeded at the ordinary temperature.

It should be added that in the Experiments 1, 2, 3, 4, and 5 the single phases of the reaction XII follow in the order *a*, *b*, whereas in Exp. 6, the order is *c*, *b*, *a*, and in Experiments 7 and 8 the order is *c*, *b*, *a*, *b*.

As regards the practical side of the question, it should be noted that the dilution used in the last four cases indicated in the table corresponds with 1 part of ammonium oxalate in 38 parts by weight of water.

Another practically important conclusion may be drawn from the above experiments.

The function of ammonium oxalate acting on thorium oxalate is a double one, one part of the ammonium oxalate serving to convert thorium oxalate into the insoluble compound  $\text{Th}_2(\text{C}_2\text{O}_4)_5(\text{NH}_4)_2 + 7\text{H}_2\text{O}$ . If we start with one molecular proportion of thorium oxalate, we see that it will be converted into  $\frac{1}{2}[\text{Th}_2(\text{C}_2\text{O}_4)_5(\text{NH}_4)_2 + 7\text{H}_2\text{O}]$ , for which purpose  $\frac{1}{2}$  mol. of ammonium oxalate will be used.

Now, on taking the last case of the table, that is, ratio XIV, as a standard, we see that, in order to obtain a stable solution of *one molecular* proportion of thorium oxalate [at the normal dilution of 1 mol.  $\text{Th}_2(\text{C}_2\text{O}_4)_2$  and 1000 of water] 3.59 of ammonium oxalate must be used. From these, in the *first* phase of the reaction, 0.5 mol. is used for the formation of the above intermediate solid compound,  $\text{Th}_2(\text{C}_2\text{O}_4)_5(\text{NH}_4)_2 + 7\text{H}_2\text{O}$ , and by the further action of

the remaining 3.09 mols. the system  $\text{Th}(\text{C}_2\text{O}_4 \cdot \text{NH}_4)_4 + 1.59(\text{NH}_4)_2\text{C}_2\text{O}_4 + 1000\text{H}_2\text{O}$  is reached, which is represented by a clear, stable solution (*second* phase).

A different state of things will take place if *the same quantity* of 3.59 mols. of ammonium oxalate is used for the dissolution of *more than* 1 mol. of thorium oxalate. Every 2 mols. of thorium oxalate will require 1 mol. of ammonium oxalate, in order to form the intermediate solid compound,  $\text{Th}_2(\text{C}_2\text{O}_4)_5(\text{NH}_4)_2 \cdot 7\text{H}_2\text{O}$  (*first* phase), so that the quantity of ammonium oxalate remaining for the completion of the *second* phase will diminish with every additional molecule of thorium oxalate present. It will be, with 2 mols. of thorium oxalate,  $3.59 - (0.5 \times 2) = 2.59$ , and the amount of thorium oxalate (or, more correctly, of the intermediate solid) dissolved will be:  $3.09 : 1 = 2.59 : x$ , from which  $x = 0.83$ , whereas 1.17 mols. will remain in the precipitate.

Therefore, on using the constant amount of 3.59 mols. of ammonium oxalate, and varying the amount of thorium oxalate, *a*, from 1 to 7 mols., the following will be the ratio between the molecular proportion of thorium oxalate dissolved, *b*, and that remaining in the insoluble precipitate, *c*.

Mols. of $\text{Th}(\text{C}_2\text{O}_4)_2 + 6\text{H}_2\text{O}$ used ( <i>a</i> ):	1	2	3	4	5	6	7
Of these are dissolved mols. ( <i>b</i> ):	1	0.83	0.67	0.5	0.33	0.17	0.02
Mols. remaining undissolved ...( <i>c</i> ):	0	1.17	2.33	3.5	4.67	5.83	6.98

*On increasing the amount of thorium oxalate, that of the ammonium oxalate remaining constant, the absolute quantity of thorium oxalate passing into solution diminishes gradually.*

The final state, given under 7, will, of course, never take place, owing to the fact that the solid compound,  $\text{Th}_2(\text{C}_2\text{O}_4)_5(\text{NH}_4)_2 + 7\text{H}_2\text{O}$ , undergoes a hydrolytic decomposition, its products being, according to the ratio XII, on the one hand, thorium oxalate and ammonium oxalate (phase *c*), and, on the other, soluble ammonium thoroxalate (phase *a*); this decomposition could not as yet be investigated quantitatively.

It is, moreover, practically important to know the quantity of thorium oxalate dissolved when an amount of 2,  $2\frac{1}{2}$ , and 3 mols. of ammonium oxalate, insufficient for complete solution, is used for 1 mol. of the former at the normal dilution. The result is the following.

Ammonium oxalate, mols.	3	$2\frac{1}{2}$	2
Thorium oxalate, mols.....	1	1	1
Percentage dissolved .....	80.9	70.1	48.5
Percentage insoluble .....	19.1	29.9	51.5

the first case is realised in Experiments 7 and 8, the third case in Experiments 1 and 2.

#### H.—*Solubility of the Tervalent Rare Earth Oxalates in Ammonium Oxalate.*

According to Bunsen (*loc. cit.*), the oxalates of the earths of the cerium and yttrium group are only to a small extent dissolved after boiling with ammonium oxalate and water and subsequent dilution with water, but no quantitative experiments, showing what amounts of these oxalates pass into solution under such conditions, have hitherto been made.

In order to obtain results comparable with those found in the case of thorium oxalate, the oxalates of different trivalent rare earths were boiled for a short time with ammonium oxalate dissolved in a very small quantity of hot water, in the same way as was done with thorium oxalate; in all cases, an excess of insoluble earth oxalate remained behind. The solution was then diluted with water, as in the experiments with thorium oxalate, so that 1 part of ammonium oxalate was dissolved in 38 parts of water.

After standing for 3 days at 20°, the clear, filtered solutions were analysed in such a way that in one part, for the sake of control, the amount of ammonium oxalate dissolved was determined volumetrically, whereas the principal portion of the solution was evaporated to dryness and the residue calcined.

As the amount of the oxalate of the earth which passes into solution is very small, the ammonium oxalate was purified by recrystallisation from hot water, and the slightly acid salt obtained was again recrystallised from hot water containing some free ammonia; the salt thus obtained left only 0.01409 per cent. of ash (K, Na), and after subtracting the corresponding amount of salt from the residue obtained on calcination, the quantity of the rare earths passing into solution was obtained.

The experiments, the numerous details of which it would be uninteresting to describe, were made with the oxalates of lanthanum, praseodymium, neodymium, cerium, and yttrium, all of which were most carefully purified by me. The yttrium material I owe to the kindness of Prof. Nilson. In the following table, the results obtained are compared with the result yielded under exactly similar conditions by thorium, and the arrangement contains the quantities in grams of earths corresponding with the different oxalates dissolved by 1 gram of ammonium oxalate, as well as their relative values, the smallest quantity obtained in the case of the most positive lanthanum being

taken as a unit. One gram of ammonium oxalate, dissolved in 38 grams of water, dissolved

	Gram.	Relative values.
$\text{La}_2\text{O}_3$ .....	$= 0.000233$	$= 1$
$\text{Pr}_2\text{O}_3$ .....	$= 0.000263$	$= 1.13$
$\text{Nd}_2\text{O}_3$ .....	$= 0.000335$	$= 1.44$
$\text{Ce}_2\text{O}_3$ .....	$= 0.000417$	$= 1.80$
$\text{Y}_2\text{O}_3$ .....	$= 0.002562$	$= 10.99$
$\text{ThO}_2$ .....	$= 0.620000$	$= 2663.00$

From the result of these experiments, the following conclusions may be drawn.

1. The solubility of the oxalates of the earths of the cerium and yttrium group in ammonium oxalate is very small as compared with that of thorium oxalate.

2. The oxalate of lanthanum, as that of the most positive or basic of all the known rare earths, is dissolved to the smallest extent, whereas that of the most negative, thorium, is very easily dissolved.

3. The less basic character of the yttrium earths is clearly shown as compared with the more basic cerite earths. In accordance with this, a mixture of the oxalates of an yttrium and gadolinium material from cerite gave the numbers  $0.00180 \text{ gram} = 7.8$ , whereas a mixture of the oxalates of a material containing erbium and holmium, and also obtained from cerite, gave  $0.00207 \text{ gram} = 8.9$ . These numbers are intermediate between those obtained for yttrium oxalate and the oxalates of the cerite metals.

4. *The tendency to form complex oxalates decreases with increasing basicity of the rare earths.*

It may be that the consequent application of the method described will give a test of purity or individuality of the rare earths.

### I. *Solubility of the Rare Earth Oxalates in Dilute Sulphuric Acid.*

It is known that the oldest method for the separation of the rare earths—introduced by Mosander—is founded on the fact that, on precipitating a solution of a mixture of earths by oxalic acid, it is generally the oxalate of the more feeble base which is thrown down first, and that of the strongest base last. As, on adding oxalic acid solution to that of a neutral salt of a rare earth metal (the sulphate, for example), the insoluble oxalate is formed and the mineral acid is liberated, the above process is closely connected with the solubility of the rare earth oxalates in mineral acids. The method was modified, for example, in separating lanthanum from old didymium, by dissolving a mixture of

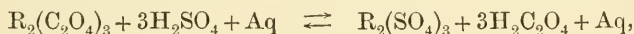


the oxalates in a warm mineral acid, and producing crystallisation by cooling; the solution contained a relatively larger amount of the more basic lanthanum, whilst the didymium accumulated in the insoluble portion.

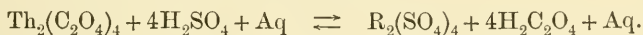
In my comparative researches on the rare earth oxalates, I tried to obtain numbers expressing relations of the above kind.

For this purpose, the purest oxalates of the rare earths which I could prepare were treated with normal sulphuric acid in such a way that as much oxalate passed into the solution as possible (that is, the solution was "saturated"), and yet an excess of undissolved oxalate still remained in the insoluble state as a "ground substance." The sulphuric acid was repeatedly shaken with the oxalate at the ordinary temperature (about 20°), and the solution analysed.

The state of the system at the beginning and at the end may be expressed by the following reversible reaction, where R represents the trivalent elements Nd, Pr, Ce, Y, La,

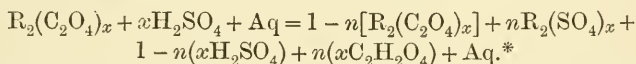


and for the quadrivalent thorium we have



(To make the results comparable, the formula of thorium oxalate is written so as to contain also two atoms of thorium.)

The reaction, in order to express the state of equilibrium, may be also written thus, where  $x = 3$  or  $4$ ,  $1 > n$ , and  $R = Th, Nd, Pr, Ce, Y, La$



The analysis was made in such a way that the oxalic acid contained in measured volumes of the clear liquid was determined with decinormal permanganate, and the numbers were regarded as definite when no increase in the solubility could be found, which was generally the case after 24 hours. The results obtained are given in the table on p. 974.

Col. I contains the formulæ of the oxalates used, regarded as anhydrous, and in order to obtain comparable results, each molecule is written so as to contain the same quantity of 2 atoms of the earth element.

Col. IIa contains the mean values of the volumes of permanganate reduced to strictly decinormal, and in *b* the relative numbers, the smallest being taken as a unit.

\* No account was taken of the circumstance that, in such a solution, intermediate products as oxalosulphates, acid sulphates and the products of their ionisation and hydrolytic decomposition may be formed, for my aim was only to obtain results which would be practically applicable.

I. Oxalate.	II. c.c. of N/10 KMnO <sub>4</sub> used for 100 c.c. of the solution.		III. Grams of oxalates de- composed by 100 c.c. of the H <sub>2</sub> SO <sub>4</sub> solution.		IV. $n$ = fraction of the mole- cule of the oxalate decomposed.	
	<i>a.</i>	<i>b.</i>	<i>a.</i>	<i>b.</i>	<i>a.</i>	<i>b.</i>
Th <sub>2</sub> (C <sub>2</sub> O <sub>4</sub> ) <sub>4</sub> ...	1.644	= 1	0.018102	= 1	0.001644	= 1
Nd <sub>2</sub> (C <sub>2</sub> O <sub>4</sub> ) <sub>3</sub> ...	10.925	= 6.6464	0.10034	= 5.5434	0.010925	= 6.6464
Pr <sub>2</sub> (C <sub>2</sub> O <sub>4</sub> ) <sub>3</sub> ...	13.552	= 8.2440	0.12327	= 6.8109	0.013552	= 8.244
Ce <sub>2</sub> (C <sub>2</sub> O <sub>4</sub> ) <sub>3</sub> ...	18.042	= 10.976	0.16360	= 9.0378	0.018042	= 10.976
Y <sub>2</sub> (C <sub>2</sub> O <sub>4</sub> ) <sub>3</sub> ...	23.424	= 14.250	0.17258	= 9.5340	0.023432	= 14.250
La <sub>2</sub> (C <sub>2</sub> O <sub>4</sub> ) <sub>3</sub> ...	28.426	= 17.534	0.25606	= 14.1455	0.028426	= 17.534

Col. IIIa contains the absolute quantities of the anhydrous oxalates decomposed by 100 c.c. of normal sulphuric acid, and *b* the relative numbers, the smallest being taken as a unit.

Col. IVa contains the fractions of the molecular quantities of the oxalates decomposed by 3 or 4 molecules of sulphuric acid. The meaning of *n* is seen from the last equation; *b* contains the relative numbers, the molecular quantity being taken as a unit.

Another series of experiments was made in such a way that the earth oxalate, taken in excess, was dissolved in normal sulphuric acid at the temperature of the water bath, and the liquid was analysed after cooling. In this case, very variable results were obtained, even with one and the same earth oxalate, owing to the circumstance that crystals of some compound separated from the solution with great slowness, so that the solution remained for a long time "supersaturated" with regard to that crystalline compound, even when the last formed the "ground substance," and was shaken with the liquid. In the case of lanthanum and yttrium, beautifully formed crystals were deposited, which required for their formation, in the well closed vessel, more than one year and a half.

In order to decide the question whether the crystals consist of an oxalosulphate or of an oxalate, both compounds were analysed.

*a.* Lanthanum compound, 0.28703 gram gave 0.13657 gram La<sub>2</sub>O<sub>3</sub> = 47.58 per cent., and 0.30105 gram gave 0.09884 gram C<sub>2</sub>O<sub>3</sub> = 33.06 per cent.

The compound has the formula La<sub>2</sub>(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub> + 7H<sub>2</sub>O.

Calculated.	Found.
La <sub>2</sub> O <sub>3</sub> = 324.4 = 48.67	47.58
3C <sub>2</sub> O <sub>3</sub> = 216.06 = 32.42	33.06
7H <sub>2</sub> O = 126.11 = 18.91	(19.36)
<hr/> 666.57 100.00	<hr/> 100.00

Hitherto, the anhydrous oxalate only has been described by Holzmänn, and the salt,  $\text{La}_2(\text{C}_2\text{O}_4)_3 + 9\text{H}_2\text{O}$ , by Czudnowicz and by Cleve.

*b.* Yttrium compound : 0.06272 gram gave 0.01922 gram  $\text{Y}_2\text{O}_3 = 30.64$  per cent., and 0.05305 gram gave 0.01511 gram  $\text{C}_2\text{O}_3 = 28.49$  per cent.

The formula is  $\text{Y}_2(\text{C}_2\text{O}_4)_3 + 17\text{H}_2\text{O}$ . Bahr and Bunsen describe the salt  $\text{Y}_2(\text{C}_2\text{O}_4)_3 + 3\text{H}_2\text{O}(9\text{H}_2\text{O})$ .

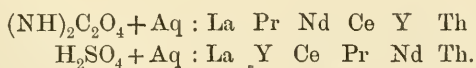
The above analyses prove that solid oxalosulphates are not formed under the conditions obtaining in my experiments, and it may be safely concluded that, even in the case of the less basic earths examined, oxalates alone form the "ground substance."

Considering the numbers contained in the above tabular arrangement, from the theoretical point of view, it should be remembered that, although the present would seem to be only a reversed case of the well-known experiments of Ostwald, who determined the affinity of different acids from the quantity of calcium oxalate decomposed by them, yet they do not even qualitatively express the relative affinities of the bases (rare earths) investigated, and they can, therefore, still less be applied for the quantitative determination of their relative affinities.

Twenty years ago, yttrium was considered by Nilson to be the most positive of all rare earth metals, because it forms the most neutral chloroplatinate,  $4\text{YCl}_3, 5\text{PtCl}_4 + 51\text{H}_2\text{O}$ , whereas the other earth metals form salts of the type  $2\text{RCl}_3, 2\text{PtCl}_4 + x\text{H}_2\text{O}$ . At the present time, lanthanum is generally considered to be the most positive earth metal, but it is remarkable that yttrium approaches lanthanum most closely in the above table. On considering, however, the behaviour of the salt solutions of the rare earth metals towards ammonia, we find that yttria is precipitated before the trivalent cerite metals, that is, it appears more negative or less basic. The same is the case when the stability of the rare earth nitrates, that is, their property of being more or less easily decomposed at a higher temperature, is considered.

It should be also remarked that the solubility of the earth oxalates in aqueous ammonium oxalate, which might be regarded as a function of the basicity of the earth, gives a different order of the series from the solubility in aqueous sulphuric acid.

Solubility in



The easy solubility of yttrium oxalate in mineral acids explains an interesting fact. On fractionally precipitating, with oxalic acid, a solution of lanthanum and old didymium containing yttrium, the yttrium

will undoubtedly follow lanthanum. The numbers found by some authors as the atomic weight of lanthanum,  $\text{La} = 133\text{--}135$  (instead of  $\text{La} = 138.2$ ) are explained by the presence of yttrium ( $\text{Y} = 89$ ).

The following practical experience is gained from the above experiments.

1.—Thorium is distinguished from the trivalent earth metals by the considerably smaller solubility of its oxalate in mineral acids. A simple method of purifying thorium from foreign earth metals may be founded upon this property, which consists in the precipitation of a hot strongly acid thorium solution by the gradual addition of oxalic acid. The process is fully described in Section O (p. 983).

2.—It is known that it is impossible to prepare pure yttrium compounds containing no neodymium by removing the latter in the form of a double sulphate with potassium, for neodymium-potassium sulphate is not totally insoluble in potassium sulphate in the presence of yttrium. A method of separating the two earth metals may be founded on the difference in the solubility of their oxalates in sulphuric acid. Indeed, I found that it is easy to remove the last portions of neodymium from yttrium preparations by fractional precipitation with oxalic acid.

3.—It is further seen, from the above table, that it would not be practicable to separate yttrium from cerium by means of oxalic acid.

The individual members of the group of the rare earths resemble each other far more closely in their chemical properties than is the case with other groups of elements. Direct methods of separation are founded only upon a few reactions by which the *quadrivalent* cerium and thorium differ from the rest of the trivalent earth metals, whereas there is *not a single* direct method by which the individual members of the trivalent earth group can be separated from each other. Even the well known "potassium sulphate method" cannot be regarded as a direct one, for, since the discovery of samarium, gadolinium, terbium, dysprosium, holmium, and other earths, forming the transition from the cerite group to the gadolinite group of earths, a sharp separation of these two groups from each other has become illusory.

The trivalent earths are distinguished from each other by a difference in basicity, by the formation of higher oxides, as I have shown in 1881, further by their atomic weights, their emission and absorption spectra, and by a series of physical properties.

A field is open to younger chemists to discover new numerical relations like the above, which would not only characterise the individual earths, but might also be useful for effecting their separation, in default of direct methods.

K.—*Action of Acids on Ammonium Thoroxalate. Semi-Acid Thorium Oxalate.*

On mixing an acid with an aqueous solution of ammonium thoroxalate containing the amount of ammonium oxalate necessary to keep the complex salt in solution, precipitates are obtained differing in character according to the conditions. For example, on pouring such a solution into hot water containing nitric acid, a colloidal precipitate is obtained which cannot be separated by filtration, whereas if the acid be poured into the thorium solution, either amorphous or crystalline precipitates are formed.

It was found that the best results were obtained with oxalic acid. On adding an aqueous (10 per cent.) solution of this acid to a solution of ammonium thoroxalate in aqueous ammonium oxalate, a micro-crystalline, white precipitate was formed which could be collected readily. It was washed first with dilute aqueous oxalic acid, then with water and alcohol, and dried in the air, well covered. The analysis gave the following result.

0.1933 gram gave, on calcination, 0.0947 gram  $\text{ThO}_2 = 48.99$  per cent.

0.2855 „ was titrated with permanganate, and yielded 0.09647 gram  $\text{C}_2\text{O}_3 = 33.44$  per cent.

A salt from another different preparation was dried at  $50^\circ$ .

0.45953 gram gave 0.22625 gram  $\text{ThO}_2 = 49.23$  per cent.

0.51867 „ „ 0.17326 „  $\text{C}_2\text{O}_3 = 33.40$  „

0.42232 „ „ 0.14114 „  $\text{C}_2\text{O}_3 = 33.42$  „

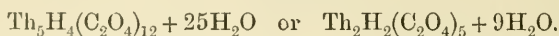
The salt is a semi-acid thorium oxalate of the formula  $2\text{ThO}_2, 5\text{C}_2\text{O}_3 + 10\text{H}_2\text{O}$  or  $2\text{Th}(\text{C}_2\text{O}_4)_2, \text{H}_2\text{C}_2\text{O}_4 + 9\text{H}_2\text{O}$  or  $\text{Th}_2\text{H}_2(\text{C}_2\text{O}_4)_5 + 9\text{H}_2\text{O}$ .

Calculated.	Found.		
$2\text{ThO}_2 = 528.90 = 49.47$	48.99	49.23	—
$5\text{C}_2\text{O}_3 = 360.10 = 33.68$	33.44	33.40	33.42
$10\text{H}_2\text{O} = 180.16 = 16.85$	—	—	—
<hr/> 1069.16 100.00			

While the present experiments were in progress, it was stated by Glaser (*Zeit. anal. Chem.*, 1897, 36, 213) that on adding *mineral acids* in excess to a solution of thorium oxalate in ammonium oxalate, the acid salt,  $\text{ThH}_2(\text{C}_2\text{O}_4)_3 + 2\text{H}_2\text{O}$ , is formed. Five months after the existence of the salt,  $\text{Th}_2\text{H}_2(\text{C}_2\text{O}_4)_5 + 9\text{H}_2\text{O}$ , was announced by me at the meeting of the British Association at Toronto (August, 1897), Glaser (*Zeit. anal. Chem.*, 1898, 37, 25) stated that his acid salt had



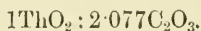
not the formula originally given to it, but he had found that a preparation obtained with hydrochloric acid (and analysed by an approximate method only) had one of the two formulæ:



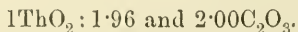
It will be seen from the following experiments that both formulæ are without foundation, and the approximate agreement of the results obtained by Glaser seems to be due merely to chance.

Hoping to obtain a still more acid salt than the above, a method of preparation and of analysis of the salt was used in which filtration and washing was entirely excluded. For this purpose, a solution of ammonium thoroxalate and ammonium oxalate, in water containing a known amount of thorium dioxide and of the oxalic acid radicle,  $\text{C}_2\text{O}_3$ , was decomposed by different acids, and the clear solution, left after the thorium present had been completely separated in the form of a precipitate, was analysed. By this indirect method, the proportion of thorium dioxide and "oxalic acid" in the precipitate was determined.

*Exp. 9.* 10.2708 grams of a solution containing, according to *Exp. 7* in Section G, in 100 parts 1.3638 parts of  $\text{ThO}_2$ , and 1.945 parts of  $\text{C}_2\text{O}_3$  was mixed with 8.5 c.c. of normal sulphuric acid at the ordinary temperature and the solution made up to 105 c.c. In the solution above the insoluble precipitate, 1.177 per cent.  $\text{C}_2\text{O}_3$  was found, so that the precipitate must contain 0.768 part  $\text{C}_2\text{O}_3$  combined with 1.3638 parts  $\text{ThO}_2$ . On dividing 1.3638  $\text{ThO}_2$  and 0.768  $\text{C}_2\text{O}_3$  by the respective molecular weights, and taking the number obtained for  $\text{ThO}_2$  as a unit, the following molecular ratio of the ingredients in the precipitate is obtained.

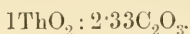


*Exp. 10.* 10.2673 grams of the solution used in *Exp. 9* was mixed with 50 c.c. of normal sulphuric acid at the ordinary temperature, and the solution made up to 100 c.c. with water. The analysis of the clear solution gave  $\text{C}_2\text{O}_3 = 1.216$  and 1.204 per cent. The precipitate contains therefore 1.364 parts  $\text{ThO}_2$  combined with 0.729 and 0.742 parts  $\text{C}_2\text{O}_3$ , from which the following molecular ratio of the constituents of the precipitate is calculated.



*Exp. 11.* 10.2652 grams of another solution containing, according to *Exp. 8*, Section G, in 100 parts 1.3320 parts  $\text{ThO}_2$ , and 1.9181 parts  $\text{C}_2\text{O}_3$  was decomposed, at a boiling temperature, with 10 c.c. of normal sulphuric acid, after which water was added to make the whole 100 c.c. The analysis of the clear solution gave  $\text{C}_2\text{O}_3 = 1.0721$  per cent., so that the precipitate contains, for 1.3320 parts of  $\text{ThO}_2$ , 0.846 part of

$C_2O_3$ . From this it follows that the molecular ratio of the constituents of the precipitate is,



From this series of experiments, it follows that, on decomposing a solution of thorium oxalate (or ammonium thoroxalate) in aqueous ammonium oxalate with a mineral acid, either the ordinary thorium oxalate is precipitated (mol. ratio  $1ThO_2 : 2C_2O_3$  as in Exp. 10) or a mixture of the ordinary oxalate with the semi-acid oxalate, in variable proportions (mol. ratio  $1ThO_2 : 2.08C_2O_3$  as in Exp. 9, or  $1ThO_2 : 2.33C_2O_3$  as in Exp. 11). This last experiment most nearly approaches the conditions of Glaser's experiments, and so it is not surprising that Glaser's numbers agree pretty closely with those calculated for an imaginary compound,  $Th_5H_4(C_2O_4)_{12} + 25H_2O$ , requiring a molecular ratio  $1ThO_2 : 2.4C_2O_3$ .

On the other hand, the formation of the "semi-acid" thorium oxalate could be observed only on decomposing the above thorium solution with oxalic acid, for, although, on adding a mineral acid to a solution containing ammonium oxalate, oxalic acid is at first set free, the "semi-acid" oxalate formed undoubtedly undergoes a more or less complete decomposition into ordinary thorium oxalate as soon as the free mineral acid is in excess. This decomposition is complete at the ordinary temperature, a finely divided precipitate being formed, but only partial at a higher temperature, when the precipitate is of a coarser nature.

An additional detailed experiment proves the correctness of the method used and of the conclusions drawn.

*Exp. 12.* 10.2459 grams of the same solution as that used in Exp. 11 was mixed, at a boiling temperature, with a solution of 30 c.c. of oxalic acid, 15 c.c. of which required 74.19 c.c. of decinormal permanganate for oxidation, and the solution was made up to 100 c.c. with water; a crystalline precipitate was formed, and 50 c.c. of the clear solution required 88.74 c.c. of decinormal permanganate for oxidation. After subtracting from this number the amount of permanganate used for the 15 c.c. (that is, 30 : 2) of oxalic acid added, thus  $88.74 - 74.19 = 14.55$  c.c., a number was obtained which, when multiplied by 2, = 29.10 c.c. represents the oxalic acid set free from the thorium solution and existing in 100 c.c. of the solution. This makes  $C_2O_3 = 1.0196$  parts in solution, and  $1.9181 - 1.0196 = 0.8985$  parts  $C_2O_3$  in the precipitate combined with 1.3320 parts  $ThO_2$ . The molecular ratio, is therefore,



\* The number found in this way is always slightly less than the truth, because in this method of analysis the unknown volume of the precipitate is neglected, so that the volume of the solution is in reality less than 100 c.c.

This ratio, found by my method of indirect analysis, completely agrees with that found by the direct analysis of the "semi-acid" salt,  $\text{Th}_2(\text{C}_2\text{O}_4)_5\text{H}_2 + 9\text{H}_2\text{O}$ .

This salt is probably an acid thoroxalate of thorium, but a normal acid oxalate of thorium cannot be obtained by the above method.

L.—*A New Thoroxalate of Thorium and Ammonium.*

In Chapter G, dealing with the hydrolytic decomposition of normal ammonium thoroxalate, Experiment 8 was described, in which 29.324 grams of pure thorium oxalate (1 mol.) was dissolved in 24.55 grams (3 mols.) of ammonium oxalate and about 900 c.c. of water. The clear liquid became turbid after a few days, and after several months the white, colloidal precipitate which formed was converted into a crystalline one; after standing for 15 months, the crystalline precipitate was collected on a small filter and washed three times very quickly with small quantities of water, as it was observed that more thorough washing would induce a decomposition resulting in the formation of a milky solution of colloidal thorium oxalate. The precipitate, after being dried at  $30^\circ$ , weighed 5.65 grams; it consisted of white, soft, smooth fibres of a silky lustre, and microscopic examination proved that it consists of needle-shaped crystals and plates, probably monoclinic.

On heating in a closed platinum crucible, the substance was found to give off, like the normal ammonium thoroxalate, considerable quantities of cyanogen, and at the same time paracyanogen was formed. At a higher temperature, pure white thorium dioxide was left.

The analysis gave the following results.

1.0914 grams, heated over the blast, left 0.5399 gram  $\text{ThO}_2 = 49.47$  per cent.

0.5428 gram yielded (with permanganate) 0.18274 gram  $\text{C}_2\text{O}_3 = 33.67$  per cent.

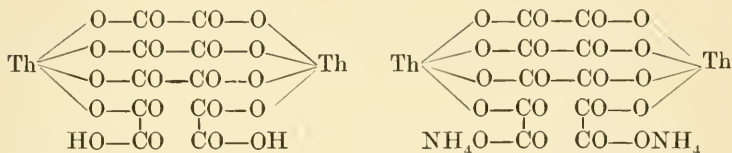
0.6247 gram, on distillation with potash, gave 0.02755 gram  $(\text{NH}_4)_2\text{O} = 4.41$  per cent.

The molecular quotients are  $1\text{ThO}_2 : 2.50\text{C}_2\text{O}_3 : 0.5(\text{NH}_4)_2\text{O}$ , and the salt has the formula,  $2\text{Th}(\text{C}_2\text{O}_4)_2 + (\text{NH}_4)_2\text{C}_2\text{O}_4 + 7\text{H}_2\text{O}$ , or



Calculated.	Found.
$2\text{ThO}_2 \dots\dots = 528.90 = 49.56$	49.47
$5\text{C}_2\text{O}_3 \dots\dots = 360.10 = 33.74$	33.67
$(\text{NH}_4)_2\text{O} \dots = 52.14 = 4.88$	4.41
$7\text{H}_2\text{O} \dots\dots = 126.11 = 11.82$	(12.05)
<hr/> 1067.25 100.00 <hr/>	<hr/> 100.00 <hr/>

This salt appears to be the ammonium derivative of the "semi-acid" thorium oxalate described in the previous chapter (which gives no cyanogen on heating), and whereas the acid salt may be regarded as an acid thoroxalate of thorium, the salt just described would contain ammonium in place of the two hydrogen atoms of the former.



M.—*Action of Nitric Acid on the Acid Thorium Oxalate and on other Rare Earth Oxalates.*

On heating acid thorium oxalate with concentrated nitric acid on a water bath, the oxalic acid which makes this compound acid (in comparison with the ordinary thorium oxalate) is first of all oxidised. At the same time, the normal thorium oxalate formed is converted into a heavy, crystalline, sandy precipitate, which resists fairly well the action of nitric acid at 100°. If it is desired to convert this oxalate into the soluble nitrate by oxidation, the salt must be *boiled* with concentrated nitric acid for a considerable length of time, as the oxidation proceeds but slowly; finally, however, a clear solution of thorium nitrate is obtained.\*

On performing the same experiment with the oxalate of a trivalent earth metal like lanthanum or cerium, it is observed that the heat of the water bath is sufficient for a comparatively quick oxidation and solution of these oxalates. Oxalates of the yttrium earths may also be converted into nitrates in the same way, although somewhat more slowly.

This behaviour permits of the following general conclusion being drawn.

The oxalates of the rare earths are the more easily oxidised by nitric acid, the greater their basicity, or the property of the oxalates of being oxidised by nitric acid decreases with the decreasing basicity of the earth (including thorium).

‡ Upon this behaviour, a method of purification of thorium from other rare earths may be founded.

To a solution of crude thorium oxalate in ammonium oxalate, which still contains a small quantity of the trivalent earths, concentrated nitric acid is added gradually; at first a colloidal precipitate is pro-

\* This fact is new, and proves that the ordinary statement, "thorium oxalate is insoluble in nitric acid," is incorrect.

duced, but on heating the mixture on a water bath, the oxalates of the tervalent rare earths, principally lanthana and ceria, contained in the precipitate are first attacked by the nitric acid, whereas the thorium compound is converted into the crystalline oxalate, which is almost insoluble in nitric acid under these conditions.

N.—*Attempts to separate Thorium from other Rare Earths quantitatively.*

The first object of the experiments described in the present paper was to find a method for the preparation of pure thorium compounds. At the same time, some experiments were started in order to see whether the differences between the solubilities of thorium oxalate and of the other earth oxalates in ammonium oxalate, which were studied from a quantitative point of view, could be applied to their quantitative separation.

My experiments were, however, given up when, at the end of 1897, the work of Hintz and Weber (*Zeit. anal. Chem.*, 36, 682) was published, in which experiments of a similar kind were described.

*Exp. 13.* 2.1372 grams of pure thorium oxalate containing 1.1094 grams  $\text{ThO}_2$  (1 mol.) was dissolved in 1.7893 grams of ammonium oxalate (3 mols.) and a small quantity of water. The clear solution was boiled with 0.4239 gram of lanthanum oxalate containing 0.19784 gram  $\text{La}_2\text{O}_3$ , and then made up to 75 c.c. with water. This gave a milky, turbid solution which could be filtered only with the greatest difficulty, and had to be poured many times through the filter in order to collect the insoluble residue; the latter, on calcination in a crucible, gave 0.3672 gram of oxides, instead of 0.1978 gram  $\text{La}_2\text{O}_3$ . This incomplete separation is due to the fact that 3 mols. of ammonium oxalate are insufficient to keep 1 mol. of thorium oxalate in solution, the presence of lanthanum oxalate producing at once what takes place only after a long time when the thorium oxalate is pure, about 19 per cent. of the thorium originally dissolved coming down with the precipitate.

*Exp. 14.* 0.5614 gram of highly purified thorium oxalate containing 0.2914 gram  $\text{ThO}_2$ , and 0.4496 gram of lanthanum oxalate containing 0.2288 gram of  $\text{La}_2\text{O}_3$  were boiled with 0.627 gram of ammonium oxalate (4 mols.) and a small quantity of water, and then diluted with much water and weighed. As the liquid could not be separated from the precipitate by filtration, weighed quantities of the clear solution were used for the determination of the quantity of the earth dissolved. This was found to be 0.20104 gram, whereas the weight of  $\text{ThO}_2$  taken was 0.2914 gram, showing that 0.0906 gram of thorium remained in the insoluble portion. The 0.20104 gram of earth dissolved still contained a small quantity of lanthanum.



This result confirms that obtained by Hintz and Weber, namely, that it is impossible to separate thorium from a cerite metal quantitatively by one treatment with ammonium oxalate; for in the presence of the oxalate of a trivalent earth a smaller quantity of thorium oxalate is dissolved than passes into solution when thorium oxalate alone is treated with the same quantity of ammonium oxalate. It seems that during this reaction insoluble thoroxalates of trivalent rare earths are formed.

### O.—On the Preparation of Pure Thorium Compounds.

*Principles of the Method.*—The study of the properties of thorium compounds, in comparison with those of the trivalent earths, have enabled me to work out a process for preparing pure thorium compounds. This consists in a combined application of the following reactions, which were studied from a quantitative point of view.

1. Thorium oxalate is remarkably less soluble in acids than the oxalates of the trivalent rare earths (Section I).

2. Thorium oxalate is far more soluble in ammonium oxalate than the trivalent earth oxalates, and 1 mol. of the former is kept in solution by 3.59 mols. of ammonium oxalate, even at a considerable dilution, a complex salt, ammonium thoroxalate, being formed. The solubility of trivalent earth oxalates in ammonium oxalate is many hundred times smaller (Section H).

3. A solution of ammonium thoroxalate in ammonium oxalate, on being decomposed with mineral acids, yields a colloidal precipitate containing variable quantities of normal thorium oxalate and semi-acid thorium oxalate (Section K).

4. On treating the precipitate obtained as in 3 with nitric acid at 100°, it is converted into the coarsely crystalline thorium oxalate, whereas the oxalates of the trivalent rare earths are, for the most part, oxidised, and pass into solution (Section M).

*Description of the Process.*—The solution of a crude thorium preparation is strongly acidified with nitric acid, and, while it is heated to boiling, a solution of oxalic acid is added drop by drop, stirring continuously. When the liquid has become clear, and the further addition of a few drops of oxalic acid does not produce any change (the solution will still be precipitated by larger quantities of oxalic acid, but if we stop at the moment described, the quantity of foreign earths carried down will be very small), the hot solution is at once poured off and the precipitate is collected on a perforated platinum plate covered with a round filter with a diameter larger by about 2 mm. than the plate, and

washed first with warm water containing a little nitric acid, and finally with very dilute cold aqueous oxalic acid. In this way, all the zirconium and the greater part of the trivalent earths are removed. It will subsequently be seen, from my paper "On the Atomic Weight of Thorium," that thorium preparations of very high purity may be obtained by the application of this process alone.

The composition of the air-dried thorium oxalate corresponds with the formula  $\text{Th}(\text{C}_2\text{O}_4)_2 + 6\text{H}_2\text{O}$ ,\* and 1 part of it (1 mol.), is treated at  $100^\circ$  with 2 parts of water and 0.96 part of ammonium oxalate ( $3\frac{1}{2}$  mols.). If the thorium oxalate is dried at a higher temperature, then for every one part of thorium dioxide contained in it (as determined by calcination) 1.88 parts of ammonium oxalate and 4—5 parts of water are used. After heating for some length of time at  $100^\circ$ , a considerable quantity of water is added (about 40 times that of the ammonium oxalate taken), and the mixture is allowed to stand in high vessels for some time in order to clear; the clear liquid is then syphoned off, as it is not always possible to separate it from the precipitate by filtration. The precipitate may be worked up with other less pure portions.

After the solution of ammonium thoroxalate has been considerably concentrated by boiling down, it is heated on a water bath and nitric acid is gradually added; a colloidal precipitate is first formed, and this is partially oxidised and dissolved, the oxidation of the single constituents of this mixture of oxalic acid and thorium oxalate, being accompanied by evolution of nitrous fumes and carbon dioxide. The process is at an end as soon as the evolution of gas bubbles has nearly ceased and the thorium oxalate is deposited as a heavy, crystalline, sandy powder.

The thorium oxalate obtained in this way is very pure and may be collected and washed in the manner already described.

In order to convert this oxalate into pure thorium nitrate, it is boiled in a covered platinum dish with an excess of concentrated nitric acid until a clear solution is obtained from which no red fumes escape on boiling; the greater portion of the nitric acid is then removed by

\* Numerous analyses of the air-dried thorium oxalate gave results agreeing with the formula  $\text{Th}(\text{C}_2\text{O}_4)_2 + 6\text{H}_2\text{O}$ .

	Calculated.	Found.
$\text{ThO}_2 =$	$264.45 = 51.19$	51.09
$2\text{C}_2\text{O}_3 =$	$144.04 = 27.88$	27.78
$6\text{H}_2\text{O} =$	$108.10 = 20.93$	21.13
	<hr/> 516.59 100.00	<hr/> 100.00

Hitherto only the dihydrate,  $\text{Th}(\text{C}_2\text{O}_4)_2 + 2\text{H}_2\text{O}$ , obtained on drying the salt at  $100^\circ$ , was known.

evaporation at  $100^{\circ}$ , and subsequently at about  $80^{\circ}$ , until crystals begin to deposit from the still strongly acid solution. The liquid is then allowed to remain at the ordinary temperature, when almost the whole is converted into large, colourless, transparent crystals of the nitrate, leaving only a small quantity of an acid mother liquor.\*

After removing the mother liquor by suction and pressure between smooth filter paper, crystals of a pentahydrated nitrate, which has not yet been described, are obtained. This salt is not hygroscopic in air of ordinary humidity, and does not lose water on standing over phosphorus pentoxide.

1.1824 gram, after heating, finally over the blast, gave 0.59075 gram  $\text{ThO}_2 = 46.41$  per cent.

1.1248 gram gave 0.52145 gram  $\text{ThO}_2 = 46.36$  per cent.

The formula of the salt is  $\text{Th}(\text{NO}_3)_4 + 5\text{H}_2\text{O}$ . Calculated  $\text{ThO}_2 = 46.34$  per cent.

The purity of the thorium compounds obtained by the use of the method described in this Section was tested and confirmed as follows.

1. By the study of the spark spectrum of the chloride, which shows how difficult it is to remove from thorium the last traces of foreign substances.

2. By the feeble incandescence of the thoria prepared from the oxide or the nitrate. This test is modern, but not absolutely conclusive without exact photometric measurements, for even impure thoria may exhibit but feeble incandescence (Compare Hintz, *Zeit. anal. Chem.*, 1898, 37, 111 and 504).

5. By the determination of the atomic weight.

The points 1 and 3 will form the subject of a separate publication, and it may here be noted that the most highly purified preparations give, for the atomic weight of thorium, the number  $\text{Th} = 232.43$  ( $\text{O} = 16$ ), which is identical with that obtained by Krüss and Nilson (*Ber.*, 1887, 20, 1675)

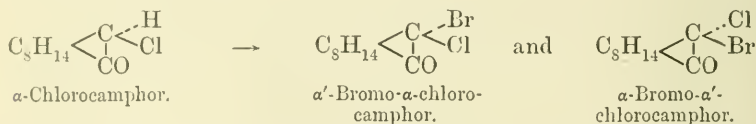
\* This method gives a purer compound than that technically applied, boiling the thorium oxalate with soda, and dissolving the washed hydroxide in nitric acid, for a nitrate prepared in this way is never free from alkali metal.

XCVIII.—*Studies of the Terpenes and Allied Compounds.*  
*Nitrocamphor and its Derivatives.* I. Stereoisomeric Chloro- and Bromo-nitrocamphors. II. Pseudo-nitrocamphor. III. Camphoryloxime (Campho-nitrophenol).

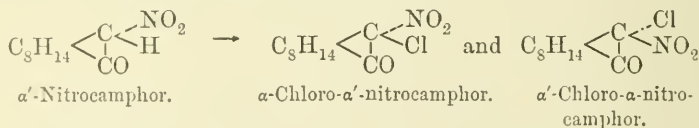
By T. MARTIN LOWRY, B.Sc.

I. STEREOISOMERIC CHLORONITROCAMPHORS and BROMONITROCAMPHORS.

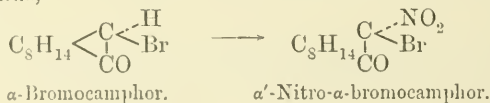
IN a recent paper on "Stereoisomeric Derivatives of Camphor" (Trans., 1898, 73, 569), I have shown that a mixture of stereoisomerides is formed by the action of bromine on  $\alpha$ -chlorocamphor, and that a similar mixture is produced by the action of sulphuryl chloride on  $\alpha$ -bromocamphor; thus,



Evidence is given in the present paper that similar mixtures are formed by the action of bromine and of chlorine on an alkaline solution of nitrocamphor; thus,



When, however,  $\alpha$ -bromocamphor and  $\alpha$ -chlorocamphor are subjected to the action of nitric acid, each appears to yield only a single nitro-derivative; thus,



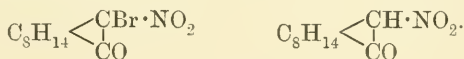
As the stereoisomeric nitro-compounds do not form isomorphous mixtures, it has been found possible to isolate each of the four compounds in a pure state; their melting points and specific rotatory powers are given in the table on the next page.

The isomerism of these compounds shows several points of contrast when compared with that of the compounds containing halogen previously described. In the case of the latter, the stereoisomerides were obtained as isomorphous mixtures which crystallised magnificently, and

	Melting point.	$[\alpha]_D$ (chloroform).
$\alpha$ -Chloro- $\alpha'$ -nitrocamphor.....	95	- 5°
$\alpha'$ -Chloro $\alpha$ -nitrocamphor.....	132	+ 13
$\alpha$ Bromo- $\alpha'$ -nitrocamphor.....	107	- 22
$\alpha'$ -Bromo- $\alpha$ -nitrocamphor .....	106	+ 53

they only differed at all largely in the one property of specific rotatory power; the isomeric chloro- and bromo-nitrocamphors, on the other hand, do not form isomorphous mixtures, and are only obtained in distinct crystals when they are almost pure, so that it is possible to isolate the less soluble isomeride by crystallising only five or six times. The melting points of the two chloronitrocamphors differ by 37°, but the difference amounts to only 1° in the case of the two bromonitrocamphors; in each case, however, a mixture of the two isomerides melts at a point about 15° lower than the mean of the separate melting points; these results may be contrasted with the behaviour of the isomeric chlorobromocamphors, the melting point of which never varies by more than 6°, whatever the proportions may be in which they are mixed. The difference in specific rotatory power between the two bromonitrocamphors amounts to as much as 75°, but is only 18° in the case of the chloronitrocamphors; the differences are, however, greater when benzene is used as a solvent instead of chloroform.

When submitted to the action of reducing agents, nitrobromo- and nitrochloro-camphor very readily lose their halogen atom and are converted into nitrocamphor:

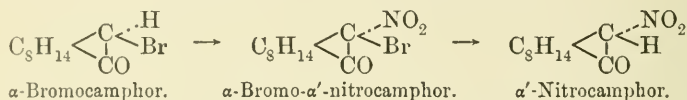


Only one nitrocamphor is produced by this action, although in several cases an impure preparation of the substance has been described as an isomeride. In the case of the bromochlorocamphors, I have shown that both stereoisomerides yield the same  $\alpha$ -chlorocamphor on reduction, although this involves the transference of the chlorine from the  $\alpha'$ - to the  $\alpha$ -position in the case of one isomeride; it is, therefore, not surprising that only one nitrocamphor should be produced by the ordinary methods of preparation.

The orientation of the radicles in nitrocamphor and its derivatives may be deduced in the following way. The  $\alpha$ -mono-derivatives of camphor are, in general, more highly dextrorotatory than camphor itself; nitrocamphor, however, is lævorotatory, and it is therefore probable that the nitro-group occupies the  $\alpha'$ - and not the  $\alpha$ -position;



ordinary nitrocamphor must, therefore, be distinguished by the name *α'*-nitrocamphor. The nitrobromo- and nitrochloro-camphors, which are intermediate products in the preparation of nitrocamphor, agree with this substance in being levorotatory, and may, therefore, also be regarded as having the nitro-group in the *α'*-position; the dextro-rotatory isomerides are consequently to be regarded as derivatives of the hypothetical *α*-nitrocamphor. This scheme of orientation allows the formation of nitrocamphor to be represented as a case of direct substitution not involving any isomeric change; thus,



*Action of Nitric Acid on α-Bromo- and α-Chloro-camphor.*

*Action of Nitric Acid on α-Bromocamphor.*—Camphoric acid and nitrobromocamphor have long been recognised as products of the action of nitric acid on *α*-bromocamphor (Schiff, *Ber.*, 1880, 13, 1402; Cazeneuve, *Bull. Soc. Chim.*, 1884, 42, 69); a third product, which appears to have been overlooked, is *αα'*-dibromocamphor, which is produced by the action of the bromine that is liberated in the oxidation to camphoric acid; the presence of this substance is to be inferred from the fact that a large amount of *α*-bromocamphor invariably separates when the product of nitration is reduced to nitrocamphor. In consequence of the formation of dibromocamphor, a considerable amount of oil is obtained in addition to solid nitrobromocamphor, and several crystallisations are required before the latter can be obtained free from this impurity; there is, however, no evidence which would suggest the presence of a second nitrobromocamphor in the oily residues. A similar case of bromination has recently been described by Lapworth and Kipping, who have shown that the chief product of the action of nitric acid on bromocamphorsulphonic acid is a dibromo-acid (*Trans.*, 1897, 71, 19; *Proc.*, 1898, 160).

In order to ascertain whether the nitrobromocamphor prepared by this method is a homogeneous substance or an isomorphous mixture, it was submitted to a series of crystallisations; it was found, however, to have a constant melting point and specific rotatory power after it had been crystallised seven times, and it may therefore be regarded as a homogeneous substance. When pure, it melts sharply and constantly at 107°; its specific rotatory power is  $[\alpha]_D = -22.0^\circ$  in a 10 per cent. solution in chloroform at 20°, and  $[\alpha]_D = -54^\circ$  in a 10 per cent. solution in benzene at 20°.

*Action of Nitric Acid on α-Chlorocamphor.*—The chief products of the

action of nitric acid on  $\alpha$ -chlorocamphor are camphoric acid and nitro-chlorocamphor, as was shown by Cazeneuve (*Bull. Soc. Chim.*, 1883, **39**, 504); no dichlorocamphor appears to be produced. If care be taken to use a preparation free from dichlorocamphor, the amount of oily matter produced in the nitration is very small, and can be still further reduced by boiling a second time with nitric acid; in this way, it is possible to convert the chlorocamphor almost completely into camphoric acid and nitrochlorocamphor, and there is no reason to suppose that any third substance is produced. The so-called " $\beta$ -nitrochlorocamphor," which is said to be present in the mother liquors, must be regarded as a mixture and not as a definite substance; its melting point is given by Cazeneuve (*Bull. Soc. Chim.*, 1888, **49**, 427) as  $98^{\circ}$ , and by Schiff and Puliti (*Ber.*, 1883, **16**, 888) as  $110^{\circ}$ , but neither description agrees with the properties of the pure chloronitrocamphors described in this paper.

The  $\alpha'$ -nitro- $\alpha$ -chlorocamphor prepared by the method described is very readily purified; indeed, its melting point and specific rotatory power were found to be constant after only four crystallisations. The pure substance melts at  $95^{\circ}$ ; its specific rotatory power is  $[\alpha]_D = -4.8^{\circ}$  in a 10 per cent. solution in chloroform at  $20^{\circ}$ , and  $[\alpha]_D = -39.2^{\circ}$  in a 10 per cent. solution in benzene at  $20^{\circ}$ .

#### *Action of Bromine and Chlorine on Nitrocamphor.*

*Action of Bromine on an Alkaline Solution of Nitrocamphor.*—By the action of bromine and chlorine on an aqueous solution of potassium nitrocamphor, Schiff obtained two substances to which he ascribed the formulæ  $C_{30}H_{43}Br_2N_3O_{11}$  and  $C_{30}H_{43}Cl_2N_3O_{11}$  (*Gazzetta*, 1881, **11**, 22); on repeating the experiments, however, I have obtained products which, even when analysed before they are purified, yield results corresponding with the simpler formulæ  $C_{10}H_{14}BrNO_3$  and  $C_{10}H_{14}ClNO_3$ ; the low percentages of halogen obtained by Schiff are probably due to the use of an insufficient amount of alkali to keep the nitrocamphor in solution. In each case, the product actually consists of a mixture of the two stereoisomerides which are theoretically possible, but as these are obtained practically free from impurity, the mixture is eminently adapted for the separation of the two isomerides.

The product of the action of bromine on a solution of nitrocamphor in an excess of potassium carbonate is a white, amorphous substance melting at  $86^{\circ}$ ; on analysis, 0.3430 gave 0.2337 AgBr, whence Br = 28.99 per cent., corresponding accurately with the formula  $C_{10}H_{14}BrNO_3$ , which requires Br = 28.97 per cent. The specific rotatory power of this product was found to be  $[\alpha]_D = +21^{\circ}$  in a 5 per cent. solution in chloroform at  $20^{\circ}$ . After crystallising five times from spirit, a fraction was obtained which melted at  $106^{\circ}$ , and by

further crystallising this from benzene, acetic acid, and spirit, fine needles were obtained melting sharply and constantly at  $107^{\circ}$ , and having a specific rotatory power  $[\alpha]_D = -21.5^{\circ}$  in a 5 per cent. solution in chloroform at  $18^{\circ}$ ; the less soluble fraction is therefore identical with the *α-bromo-α'-nitrocamphor* which is produced by the action of nitric acid on *α-bromocamphor*. After a long series of fractionations, a crystalline product was also isolated from the mother liquors; this melted at  $90^{\circ}$ , and its specific rotatory power was  $[\alpha]_D = +33^{\circ}$  in chloroform solution. By crystallising from dilute spirit, the melting point was raised to  $98^{\circ}$ , and after four more crystallisations from spirit and acetic acid it was  $106^{\circ}$ , but after this no further change of melting point was produced by three more crystallisations from spirit and light petroleum. *α'-Bromo-α-nitrocamphor*, the more soluble constituent of the mixture, melts therefore quite constantly at  $106^{\circ}$ ; its specific rotatory power was found to be  $[\alpha]_D = +53^{\circ}$  (approximately) in a 0.5 per cent. solution in chloroform. The melting point only differs by  $1^{\circ}$  from that of the stereoisomeride, but a mixture of the two substances melts at about  $90^{\circ}$ ; the specific rotatory powers of the two substances in solution in chloroform differ by  $75^{\circ}$ .

Ordinary *α-bromo-α'-nitrocamphor*, melting at  $105^{\circ}$ , was also obtained by warming a solution of nitrocamphor in acetic acid to  $100^{\circ}$  with an excess of bromine, and crystallising the product four times from spirit; probably both stereoisomerides are formed, but the method yields an impure product which is unsuitable for fractionation.

*Action of Chlorine on an Alkaline Solution of Nitrocamphor.*—The product of the action of chlorine on a solution of nitrocamphor in an excess of potassium carbonate is a white, amorphous solid melting at  $116^{\circ}$ ; on analysis, 0.3502 gave 0.2181 AgCl, whence Cl = 15.40 per cent. (calc. 15.31 per cent.), corresponding closely with the formula  $C_{10}H_{14}ClNO_3$ ; its specific rotatory power was found to be  $[\alpha]_D = +5.5^{\circ}$  in a 5 per cent. solution in chloroform at  $14^{\circ}$ . After crystallising four times from spirit, it was obtained in distinct crystals melting at  $132^{\circ}$ , and no further change of melting point was effected by four more crystallisations from spirit, light petroleum, and acetic acid. The substance thus isolated is not identical with the *α-chloro-α-nitrocamphor* produced by the action of nitric acid on *α-chlorocamphor*, and is, therefore, to be regarded as the stereoisomeric *α'-chloro-α-nitrocamphor*; its specific rotatory power was found to be  $[\alpha]_D = +13^{\circ}$  in a 4 per cent. solution in chloroform at  $20^{\circ}$ , and  $[\alpha]_D = +19^{\circ}$  in a 3 per cent. solution in benzene at  $19^{\circ}$ . The melting points of the two isomerides differ by  $37^{\circ}$ , their specific rotatory powers differ by  $18^{\circ}$  in solution in chloroform, and by  $58^{\circ}$  in solution in benzene; a mixture of the two substances melts at about  $100^{\circ}$ . No attempt was made to isolate the *α-chloro-α'-nitrocamphor*, which forms

the more soluble constituent of the mixture, but it appears to be present in the initial product to the extent of rather more than one-half.

*Reduction of Nitrobromo- and Nitrochloro-camphor.*

*Reduction of Nitrobromocamphor.*—Nitrocarnphor was first prepared by Schiff (*Ber.*, 1876, 13, 1403) by reducing nitrobromocamphor with alcohol and potash, but the product described by him appears to have been impure. The pure substance melts at  $102^{\circ}$ , and yields an anhydride melting at  $190^{\circ}$  with evolution of gas (see this vol., p. 996); the permanent value of the specific rotatory power is  $[\alpha]_D = -104^{\circ}$  in a 5 per cent. solution in benzene at  $15^{\circ}$ .

*Reduction of Nitrochlorocamphor.*—By the action of a zinc-copper couple on an alcoholic solution of nitrochlorocamphor, Cazeneuve obtained an " $\alpha$ -nitrocarnphor" melting at  $100$ – $101^{\circ}$ , and having a specific rotatory power  $[\alpha]_D = -102^{\circ}$  in a 5.2 per cent. solution in benzene (*Bull. Soc. Chim.*, 1887, [ii], 47, 920). These constants agree closely with those of the  $\alpha'$ -nitrocarnphor described above, and the anhydride of the substance has also been described by Cazeneuve under the incorrect name of "nitrosocarnphor" (*Bull. Soc. Chim.*, 1889, [iii], 1, 558). The so-called " $\beta$ -nitrocarnphor" melting at  $97^{\circ}$ , which was obtained from the mother liquors of the above preparation, must be looked upon as merely an impure form of  $\alpha'$ -nitrocarnphor, and appears indeed to have been so regarded by Cazeneuve.

A second " $\beta$ -nitrocarnphor" melting at  $83^{\circ}$  was obtained by Cazeneuve by the action of sodium on a solution of nitrochlorocamphor in toluene (*Bull. Soc. Chim.*, 1889, [iii], 2, 707). I have also prepared this substance, and find that, when purified, it melts at  $102^{\circ}$ , and yields an anhydride melting at  $190^{\circ}$ ; it is therefore identical with ordinary  $\alpha'$ -nitrocarnphor.

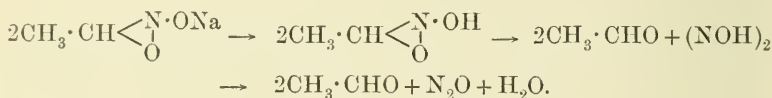
It appears, therefore, that only a single nitrocarnphor is produced on reducing nitrobromo- and nitrochloro-carnphor.

## II. PSEUDONITROCAMPHOR.

Until recently, it was supposed that the salts of the nitroparaffins were formed by the direct displacement of hydrogen, as represented by such a formula as  $\text{CH}_3 \cdot \text{CHNa} \cdot \text{NO}_2$ . Dr. Armstrong was, I believe, the first to suggest that this might not be the case, and that the salts are perhaps derived from an isodynamic form of the nitro-compound in which the hydrogen atom of a hydroxyl-group is displaceable by metals (*Proc.*, 1892, 101). This conclusion has since been satisfactorily established by the discovery of a number of chemical changes ex-

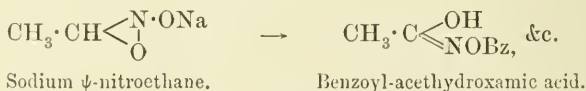
hibited by the majority of primary and secondary nitroparaffins which cannot readily be explained by the use of a 'normal' nitro-formula.

The conversion of the nitroparaffins into the corresponding aldehyde or ketone was first pointed out by Nef (*Annalen*, 1894, 280, 263), who showed that the amount of the nitroparaffin obtained on acidifying a solution of sodium nitroethane or sodium nitropropane never exceeds 25 per cent. of the theoretical quantity, whilst under ordinary conditions a complete decomposition occurs into nitrous oxide and aldehyde or acetone. If the formula proposed by Hantzsch for the isodynamic form of the nitroparaffins be adopted, their decomposition may be represented thus,

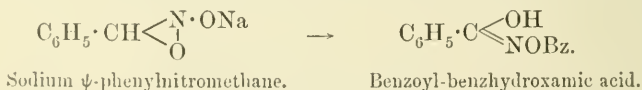


The formation of ketonic products has also been observed by Konowaloff in the case of diphenylnitromethane,  $(\text{C}_6\text{H}_5)_2\text{CH} \cdot \text{NO}_2$ , and exonitromesitylene,  $(\text{CH}_3)_2\text{C}_6\text{H}_3 \cdot \text{CH}_2 \cdot \text{NO}_2$ , (*Ber.*, 1896, 29, 2193).

An action of still greater interest is that by which the nitroparaffins are converted into derivatives of the isomeric hydroxamic acid. Thus, by the action of benzoic chloride on sodium nitroethane, Nef and Jones have obtained a large number of derivatives of acet-hydroxamic acid (*Ber.*, 1896, 29, 1218; *Amer. Chem. Journ.*, 1898, 20, 1):



The production of hydroxamic acid derivatives has also been observed in the benzenoid series by Holleman (*Rec. Trav. Chim.*, 1896, 15, 356), who obtained the benzoate of benzhydroxamic acid by the action of benzoic chloride on sodium phenylnitromethane:

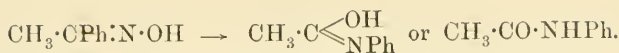


The fundamental change involved in all these cases is that represented by the formulæ



this change is precisely analogous to that which has been shown by Beckmann to occur in the case of the oximes, as will be obvious on comparing the formulæ given above with those for a typical oxime,





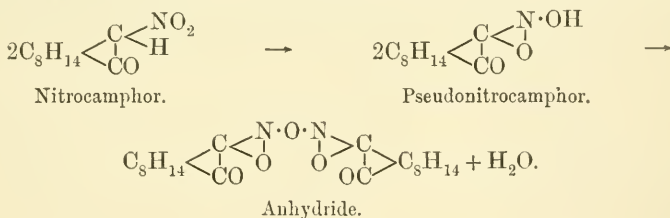
Acetophenone-oxime.

Acetanilide.

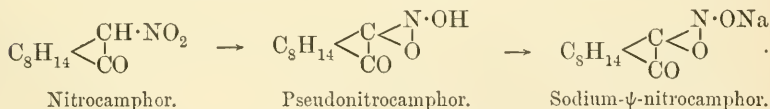
The term intramolecular oxidation has been introduced by Nef to explain the transference of an oxygen atom which attends these isomeric changes in the case of the nitroparaffins, but there does not appear to be any advantage to be derived from the use of a special nomenclature, and, moreover, the use of this term entirely masks the analogy to which attention is here directed.

The investigation of nitrocamphor has proved to be of peculiar interest from the point of view discussed in these introductory remarks, as I have been able to prepare from it derivatives of all the above types, in addition to an anhydride which constitutes an entirely new type of derivative,\* moreover, the optical activity of the substances has rendered it possible to study the change from the normal to the pseudo-type and *vice versa*, not only in the derivatives, but also in the case of the nitro-compound itself. The results obtained may be briefly summarised as follows.

1. When heated on a water bath during several hours, nitrocamphor yields an *anhydride*, as may be represented by the following formulæ.

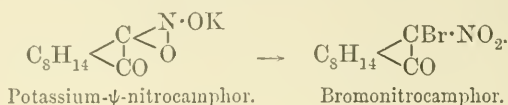


This anhydride differs in a striking manner from nitrocamphor, in that the former is very highly dextrorotatory, and a similar difference exists in the case of the salts, which are likewise dextrorotatory (Cazeneuve, *Bull. Soc. Chim.*, 1888, 49, 92); the formation of the latter may be represented by the formulæ,

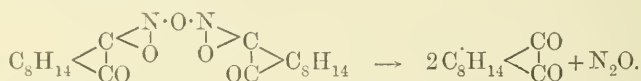


\* By the action of phenyl isocyanate on  $\psi$ -phenylnitromethane, Hantzsch and Schultze (*Ber.*, 1896, 29, 2251) obtained diphenylcarbamide, indicating that water had been withdrawn from the nitro-compound; the other product of the action, which was not purified, is perhaps an anhydride of the type described in this paper, but the formula suggested for it by Hantzsch and Schultze was  $\text{C}_6\text{H}_5 \cdot \text{C} \begin{smallmatrix} \text{N} \\ \text{O} \end{smallmatrix}$ .

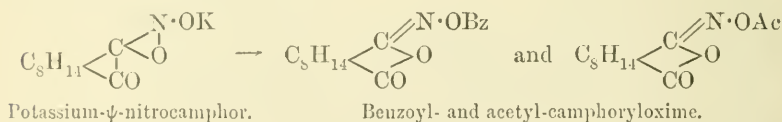
2. The reverse change from the pseudo- to the normal type occurs on acidifying solutions of the salts, when normal nitrocamphor is readily reproduced. In a similar manner, the action of chlorine and of bromine on a solution of the potassium salt gives rise to the normal nitro-compounds previously described in Section I.



3. Camphorquinone, the *ketone* corresponding to nitrocamphor, is readily obtained by the action of alcoholic potash on the anhydride, or by merely heating the latter to 190°. The decomposition may be represented by the equation

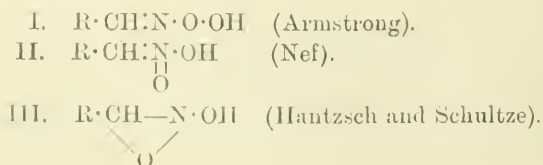


4. As nitrocamphor is a secondary nitro-compound, it cannot be converted into an isomeric hydroxamic acid such as is produced in the case of the primary nitroparaffins; a somewhat similar isomeric change, however, takes place in the preparation of an acetate or a benzoate from pseudonitrocamphor, as the substances produced are derived from camphoryloxime, a *hydroximic acid* isomeric with nitrocamphor, as may be represented by the formulæ



Camphoryloxime can also be prepared directly from nitrocamphor by means of hydrogen chloride, and has been described by Cazeneuve under the name of 'camphonitrophenol' (*Bull. Soc. Chim.*, 1889, [iii], 1, 243), although the structure which he ascribed to the substance is incorrect; this action affords an example of direct isomeric change, such as has not been observed in the case of the nitroparaffins.

Three formulæ have been suggested as representing the constitution of the pseudonitroparaffins, namely,



Of these three, that proposed by Hantzsch is to be preferred, in that it represents one oxygen atom as being already linked to carbon, and so affords the readiest explanation of the formation of compounds such as the ketones and hydroxamic acids in which a  $\text{-CO-}$  group is present. Two additional arguments can be deduced in favour of this type of formula for pseudonitrocampfor: first, the extremely high rotatory power of the substance is most readily explained by a

formula such as  $\text{C}_8\text{H}_{14}\text{C} \begin{smallmatrix} \nearrow \text{N}\cdot\text{OH} \\ \searrow \text{O} \\ \text{CO} \end{smallmatrix}$ , in which the  $\alpha$ -carbon atom is

asymmetric, rather than by a formula in which this asymmetry does

not occur, as in  $\text{C}_8\text{H}_{14}\text{C} \begin{smallmatrix} \nearrow \text{C}\cdot\text{NO}\cdot\text{OH} \\ \searrow \text{CO} \end{smallmatrix}$ . Secondly, the decomposition of

the anhydride of pseudonitrocampfor by heat into camphorquinone and nitrous oxide cannot be explained in any simple way except by the use of a formula such as that already given for the substance, in which one oxygen atom is shown to be attached to the  $\alpha$ -carbon atom.

#### *Preparation and Properties of Nitrocampfor.*

Nitrocampfor can be readily prepared in quantity in the following manner: 1000 grams of bromine are gradually mixed with 960 grams of camphor contained in a flask which is heated on a water bath, the hydrogen bromide being led off through a tube of large diameter to a tower packed with moistened coke; when all the bromine has been introduced, a solution of caustic soda is added to remove hydrogen bromide, and the product is then poured into a large quantity of water. The crude bromocampfor is boiled in large flasks with nitric acid (sp. gr. = 1.4) during about 50 hours, and the acid liquor is then poured off and evaporated, in order to recover the large amount of camphoric acid which is dissolved in it. The oily product from which the acid was separated consists mainly of a mixture of dibromocampfor and nitrobromocampfor, and, if care be taken to free it from all traces of acid substances, it can be reduced without further purification. To effect the reduction, 50 grams of the substance are warmed in a flask with 100 c.c. of spirit until nearly dissolved, and 50 c.c. of a strong solution of potash ( $\text{KOH} : \text{H}_2\text{O} = 1 : 1\frac{1}{2}$ ) are gradually added, care being taken that the contents of the flask do not boil over; after a few minutes, the reduction is complete, and the reddish-brown liquid is then poured into water and left overnight to allow of the separation of monobromocampfor. The alkaline solution, after being filtered, is acidified with hydrochloric acid in order to precipitate the nitrocampfor which separates as an oil, but after a day or two deposits crystals; these

are collected on a filter, washed thoroughly with water and spirit, and finally crystallised from spirit. A further crop of crystals can be obtained by redissolving the oily residue in potash solution, and again acidifying after the solution has been freed from neutral impurities by extracting with ether. In this way, about 13 parts of nitrocamphor can be obtained from 100 parts of camphor, half the bromocamphor being oxidised during the operation, and one-sixth recovered, whilst the remainder is for the most part converted into nitrocamphor. The fact that only about one-third of the nitrocamphor produced can be obtained in the crystalline state can be explained by the presence of both the normal and the pseudo-form in the oil, in addition to small quantities of impurities.

Nitrocamphor, when purified by repeated crystallisation, melts at  $102^{\circ}$ , but softens before melting, and when cooled again solidifies in an amorphous, and not in a crystalline, form. Its specific rotatory power is very sensitive to small changes of conditions, and only attains a constant value some hours after preparing the solution; in characterising the substance, the constant specific rotatory power of a 5 per cent. solution in benzene may be used; in such a solution  $[\alpha]_D = -104^{\circ}$  at  $15^{\circ}$ . The best way to characterise nitrocamphor is, however, by converting it into the anhydride, which is very readily prepared and purified; this decomposes and melts at  $190^{\circ}$ , and its specific rotatory power is  $[\alpha]_D = +187^{\circ}$  in a 5 per cent. solution in benzene.

#### *Anhydride of Pseudonitrocamphor.*

When a solution of nitrocamphor is evaporated to dryness on a water bath, the fused substance gradually becomes solid and opaque, owing to the formation of an anhydride of pseudonitrocamphor. The product is purified by digesting it with a small amount of spirit, and then crystallising from boiling spirit, in which it dissolves to a small extent only; on cooling, it separates at once in minute crystals.

The pure anhydride decomposes and melts at  $190^{\circ}$ , giving off a considerable amount of gas; in a 5 per cent. solution of the substance in benzene at  $21^{\circ}$   $[\alpha]_D = +187^{\circ}$ , whilst in a chloroform solution  $[\alpha]_D = +167^{\circ}$ . This high dextrorotatory power is in marked contrast with the levorotatory power of the nitrocamphor from which the substance is prepared, and in this respect it resembles the salts, which are also dextrorotatory: for example, the specific rotatory power of the anhydrous potassium salt is  $[\alpha]_D = +205^{\circ}$  in a 10 per cent. aqueous solution. The anhydride is only slightly soluble in boiling spirit, but dissolves readily in benzene, chloroform, and acetone; it is moderately soluble in ethylic acetate and acetic acid, but does not dissolve in

light petroleum to any extent. The following results were obtained on analysis.

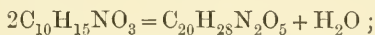
- I. 0.3391 gave 21.8 c.c. of moist nitrogen at 19° and 767mm. N = 7.78.  
 II. 0.4332 „ 28.2 c.c. „ „ 21° „ 760mm. N = 7.50.  
 III. 0.1650 „ 0.3858 CO<sub>2</sub> and 0.1138 H<sub>2</sub>O. C = 63.77; H = 7.68.  
 C<sub>20</sub>H<sub>28</sub>N<sub>2</sub>O<sub>5</sub> requires C = 63.83; H = 7.47; N = 7.47 per cent.

In order to confirm the formula found by analysis, the molecular weight was determined in a solution in benzene by the boiling-point method. When dissolved in 11.10 grams of benzene,

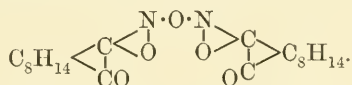
2.8487 grams raised the b. p.	2.011°.	M = 377.
1.8842 „ „	1.214°.	M = 372.
1.9012 „ „	1.191°.	M = 382.
Mean ...	...	<u>M = 377.</u>

Calculated for C<sub>20</sub>H<sub>28</sub>N<sub>2</sub>O<sub>5</sub> ... M = 376.

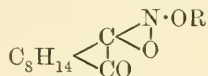
The substance is therefore an *anhydride* of nitrocamphor,



but it must necessarily be derived from a hydroxylic modification, and may therefore be represented by the formula



Its high dextrorotatory power indicates that it has a constitution similar to that of the salts of nitrocamphor, and these may therefore be represented by the formula



Pseudonitrocamphor anhydride appears to have been already prepared and examined by Cazeneuve, who devotes a whole paper to its description under the incorrect name of “*nitrosocamphor*,” C<sub>10</sub>H<sub>15</sub>NO<sub>2</sub>, (*Bull. Soc. Chim*, 1889, [iii], 1, 558); he obtained it by the action of the zinc-copper couple on nitrochlorocamphor, following the method used in preparing nitrocamphor, but evaporating to dryness at one stage of the operation. Cazeneuve gives the melting point of his product as 180°, and its specific rotatory power as [α]<sub>D</sub> = +195° in a solution in benzene; these values agree fairly well with those given above for the anhydride, and the identity of the two products is shown by other details of the description, as, for instance, in the statement that the



substance acquires a greenish-yellow tint on exposure to bright sunlight.

The anhydride is readily oxidised by nitric acid (sp. gr. = 1.42), and is thus converted into camphoric acid, melting at 182°.

### *Production of Camphorquinone.*

In order, if possible, to effect the reconversion of the anhydride into nitrocamphor, an attempt was made to hydrolyse it by means of alcoholic potash. On warming the anhydride with absolute alcohol and then adding a strong solution of potash, a vigorous action took place and the anhydride dissolved; the liquid, on being diluted with water and allowed to cool, deposited yellow needles, which, after being crystallised thrice from spirit and then sublimed, were obtained in slender needles; the substance melted at 198°, and had the characteristic sweet smell and splendid yellow colour of *camphorquinone*. No nitrocamphor is produced, and the anhydride appears to be entirely converted into camphorquinone according to the equation  $C_{20}H_{28}N_2O_5 = 2C_{10}H_{14}O_2 + N_2O$ .

It has already been mentioned that pseudonitrocamphor decomposes suddenly when heated to 190°, and an attempt was therefore made to isolate the products of decomposition. On gently heating the substance, it melted and gave off a large quantity of colourless gas, probably nitrous oxide, together with traces of brown, nitrous fumes, and a yellow, semi-solid distillate was obtained; this, on being drained on porous earthenware, crystallised from spirit, and sublimed, gave a sublimate consisting largely of camphorquinone, but this was mixed with a colourless substance; the quantity of material, however, was not sufficient to allow of a complete separation of the two. A similar result was obtained when the anhydride was merely heated to the point of decomposition and then distilled in a current of steam.

Camphorquinone, it may here be pointed out, is very readily produced from nitrocamphor and its derivatives; it has been shown by Lapworth (Trans., 1896, 69, 3) to be a product of the destructive distillation of nitrobromo- and nitrochloro-camphor, as can readily be shown by heating a little of the nitro-compound with a particle of sodium in a test tube; the yellow coloration which is acquired by an alcoholic solution of bromonitrocamphor, when exposed to air and light, is also due to camphorquinone, which I have been able to isolate from the altered substance in fine, yellow needles. The greenish-yellow tint and sweet smell which are developed on exposing pseudonitrocamphor anhydride to bright sunlight are also probably due to the formation of traces of camphorquinone.

*Benzoyl- and Acetyl-camphoryloximes.*

*Preparation of a Benzoate from Nitrocamphor.*—In order to obtain additional evidence of the presence of a hydroxyl group in pseudo-nitrocamphor, an attempt was made to prepare its benzoate. Nitrocamphor (20 grams) was dissolved in potash, and an excess of benzoic chloride added to the solution; the limpid oil thus obtained, after standing overnight, became thick and doughy, and on macerating the dough with spirit, crystals were obtained which, when purified by crystallising four times from spirit, melted sharply and constantly at  $138^{\circ}$ . The specific rotatory power of the benzoate was found to be  $[\alpha]_D = +9.3^{\circ}$  in a 5 per cent. solution in chloroform at  $15^{\circ}$ ; on analysis,

0.1979 gave 0.4874  $\text{CO}_2$  and 0.1178  $\text{H}_2\text{O}$ .  $\text{C} = 67.2$ ;  $\text{H} = 6.63$ .

$\text{C}_{17}\text{H}_{14}\text{NO}_5$  requires  $\text{C} = 67.7$ ;  $\text{H} = 6.31$  per cent.

In its properties, this benzoate agrees with that prepared in a similar way from camphoryloxime, the hydroximic acid isomeric with nitrocamphor (see Section III), and its formation from nitrocamphor involves, therefore, an isomeric change similar to those described by Nef and Jones, and by Holleman in the case of the primary nitro-paraffins.

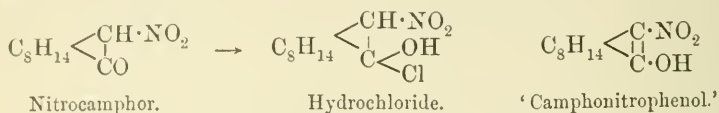
*Preparation of an Acetate from Nitrocamphor.*—When 5 grams of nitrocamphor were warmed with acetic anhydride and fused sodium acetate, a considerable rise of temperature occurred, and, on adding water, the acetate was obtained as a dirty, yellow precipitate. When crystallised four times from spirit, it melted at  $115^{\circ}$ , and its specific rotatory power was found to be  $[\alpha]_D = +6.7^{\circ}$  in a 5 per cent. solution in chloroform at  $21^{\circ}$ ; it is, therefore, identical with the acetate of camphoryloxime (p. 1002). The formation of the acetate of the isomeric hydroximic acid by this method is of interest as showing that it is not necessary to use an acid chloride in order to bring about this type of isomeric change.

Besides studying nitrocamphor in the manner described in this paper, the changes of rotatory power exhibited by nitrocamphor in various solutions have been fully investigated, and I shall be able to show that the normal and pseudo-forms of the substance are isodynamic, and that they exist together in equilibrium in solution, and in the fused state; full particulars will be published in a subsequent paper.

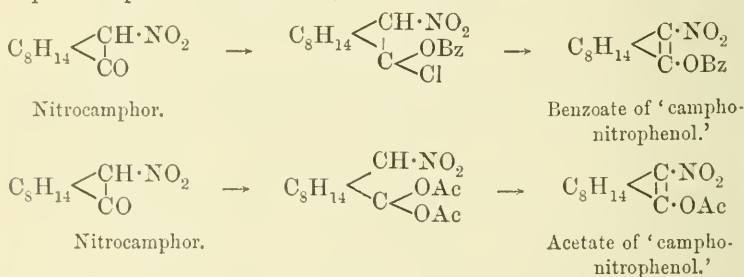
## III. CAMPHORYLOXIME (CAMPHONITROPHENOL).

"Camphonitrophenol" was prepared by Cazeneuve by boiling nitrocamphor with concentrated hydrochloric acid (*Bull. Soc. Chim.*, 1889, [iii], 1, 417); a hydrochloride is first formed (*ibid.*, p. 243), which

subsequently loses a molecule of hydrogen chloride, yielding an isomeride of nitrocamphor. This action was explained by Cazeneuve by means of the following formulæ ;



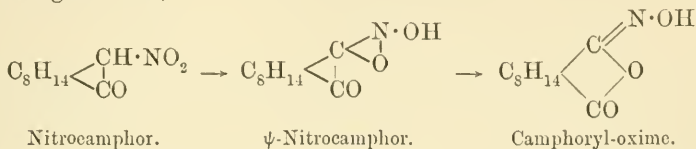
As previously pointed out (*ante*, p. 999), I have found that the benzoate and acetate of 'camphonitrophenol,' are produced in a similar manner from nitrocamphor, when the latter is acted on by benzoic chloride and potash, or by acetic anhydride and fused sodium acetate. Both of these changes can readily be explained by formulæ similar to those used by Cazeneuve to represent the preparation of 'camphonitrophenol' itself, thus,



But, although Cazeneuve's formula is admirably adapted to explain the preparation of the substance from nitrocamphor, it does not give an adequate representation of its properties ; the formula assigned to it is that of an unsaturated tertiary alcohol, but actually it behaves as a saturated compound, and decolorises neither bromine water nor potassium permanganate solution ; moreover, it possesses marked acid properties, and there is no reason to suppose that an alcohol of the above formula would behave in any such way. A further objection to Cazeneuve's formula is found in the fact that it represents merely the 'enolic' form of nitrocamphor, which the substance might, therefore, be expected to resemble in many of its interactions ; 'camphonitrophenol,' however, is perfectly stable, and cannot be reconverted into either nitrocamphor or any of its immediate derivatives. The formula proposed by Lapworth and Kipping (*Trans.*, 1897, 69, 309), which represents the substance as the stereoisomeride of nitrocamphor, is open to similar objections.

In order to arrive at a satisfactory formula for 'camphonitrophenol,' it is necessary to start from the *pseudo*-form of nitrocamphor, from which the salts and anhydride are derived (*ante*, p. 993), and not from the normal formula. Nitrocamphor is a secondary nitro-com-

pound, and it cannot, therefore, change into an isomeric hydroxamic acid in the manner observed by Nef and Jones in the case of the primary nitroparaffins (*Ber.*, 1896, 29, 1218); an analogous change may, however, be supposed to occur, such as is represented by the following formulæ,

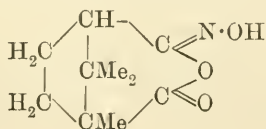


The product is thus represented as a hydroxamic acid derived from camphoric anhydride by displacing an oxygen atom by the group  $\text{=N} \cdot \text{OH}$ . This view of the nature of the isomeric change receives confirmation from the fact that isonitrosocamphor, which differs only in the absence of one oxygen atom, is known to pass into the isomeric camphorylimide when acted on by sulphuric acid or concentrated hydrochloric acid (Claisen and Manasse, *Annalen*, 1893, 274, 73):

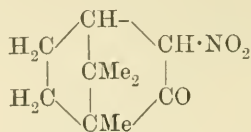


I have been able to verify the formula here suggested for campho-nitrophenol by hydrolysing it into camphoric acid and hydroxylamine, and have also been able to prove its identity with the oxime prepared synthetically from camphoric anhydride.

A second possible structure for the oxime is that represented by the formula  $\text{C}_8\text{H}_{14} \begin{array}{c} \diagup \text{CO} \\ \diagdown \text{CO} \end{array} \text{N} \cdot \text{OH}$ ; the two formulæ differ in the same way as those which have been suggested for phthalyl chloride and for phthalyl imide, in which cases, however, it is a matter of great difficulty to distinguish between the alternative formulæ. If, however, we adopt Brecht's formula for camphoric anhydride, it appears probable that the point of attack, as in the case of other ketones, would be the  $>\text{CH} \cdot \text{CO} \cdot$  group, of which an 'enolic' form is possible; the first product of the action of hydroxylamine would then be the additive compound,  $\begin{array}{c} \text{NH} \cdot \text{OH} \\ >\text{CH} \cdot \text{C}(\text{OH}) \cdot \end{array}$ , which, by loss of a molecule of water, would yield the oxime represented by the formula,



As a further consequence, it may be pointed out that nitrocamphor would then be represented by the formula,



and the tertiary " $\beta$ "-position occupied by hydrogen in camphor and by bromine in  $\alpha\beta$ -dibromocamphor would then be adjacent to the  $-\text{CH}_2-$  of the  $-\text{CH}_2\cdot\text{CO}-$  group, as represented by the first of the two formulæ given for the substance in a recent paper (Trans., 1898, 73, 577).

#### *Preparation and Properties of "Camphonitrophenol."*

When nitrocamphor is boiled with concentrated hydrochloric acid, a vigorous action takes place, the greater part of the substance passing into solution; the 'camphonitrophenol' is isolated by evaporating the acid liquors to dryness, and crystallising from water (Cazeneuve). In order to obtain the anhydrous substance, these crystals, after being dried at  $100^\circ$ , are crystallised from dry ether, when the 'camphonitrophenol' separates in large, transparent crystals. In order to establish the identity of various preparations, I have made a careful determination of the constants of the anhydrous substance; it melts at  $223^\circ$ , but chars slowly at this temperature, and in determining the melting point, it is advisable not to immerse the substance in the acid bath until the latter is within a few degrees of this temperature; the specific rotatory power is  $[\alpha]_D = +7.0^\circ$  in a 5 per cent. solution in benzene at  $14^\circ$ .

The *benzoate* is readily prepared by the action of benzoic chloride in presence of potash (Cazeneuve); when purified by crystallising four times from spirit, it melts at  $138^\circ$ , and its specific rotatory power is  $[\alpha]_D = +9.3^\circ$  in a 5 per cent. solution in chloroform at  $16^\circ$ .

The *acetate* was obtained by Cazeneuve by means of acetic chloride, but can also be conveniently prepared by warming with acetic anhydride and fused sodium acetate; when purified, it melts at  $115^\circ$ , and its specific rotatory power is  $[\alpha]_D = +6.7^\circ$  in a 5.5 per cent. solution in chloroform at  $21^\circ$ .

"*Tricamphonitrophenol.*"—Cazeneuve found that when nitrocamphor was acted on by hydrochloric acid in alcoholic solution, a substance very similar to 'camphonitrophenol' was formed, and to this he gave the formula  $(\text{C}_{10}\text{H}_{15}\text{NO}_3)_3 + 3\text{H}_2\text{O}$ ; the evidence for this formula is, however, based entirely on the analysis of a barium salt, which gave the empirical formula  $\text{C}_{30}\text{H}_{43}\text{N}_3\text{O}_9\text{Ba} + 3\text{H}_2\text{O}$ , and no attempt was made



to prove the polymeric nature of the substance by physical methods. It appears to be more probable that the substance, if it exists, represents the stereoisomeric oxime, as it yields an acetate and a benzoate identical with those prepared from camphoryloxime. Up to the present, however, I have not been able to prepare this compound, and the action of hydrochloric acid on nitrocamphor in alcoholic solution has invariably led to the production of "camphonitrophenol."

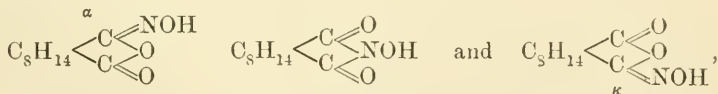
*Action of Hydrogen Chloride on Nitrocamphor dissolved in Ether.*—By passing hydrogen chloride into a solution of nitrocamphor in ether, a viscous oil was obtained which deposited crystals after standing several days in a desiccator; after purification by crystallising from ether, it was obtained in needles melting at  $223^{\circ}$ ; its specific rotatory power was found to be  $[\alpha]_D = +7.0^{\circ}$  in a 5 per cent. solution in chloroform at  $19^{\circ}$ . The product of this action is, therefore, anhydrous 'camphonitrophenol,' but the isomeric change by which it is produced takes place here at ordinary temperatures, and without the presence of water.

*Oxidation of "Camphonitrophenol."*—'Camphonitrophenol' is very easily oxidised by boiling with 50 per cent. nitric acid; the product consists of camphoric acid, which melts at  $182^{\circ}$ , and is readily converted into the anhydride melting at  $218^{\circ}$ .

*Hydrolysis of "Camphonitrophenol."*—As it was considered possible, on theoretical grounds, that 'camphonitrophenol' might have the constitution of an oxime of camphoric anhydride, an attempt was made to hydrolyse it to hydroxylamine and camphoric acid. For this purpose, 10 grams of the substance were heated in a sealed tube during 4 hours at  $140^{\circ}$ , together with 20 grams of concentrated hydrochloric acid; the solid product had all the properties of camphoric acid, and was further characterised by converting it into the anhydride melting at  $218^{\circ}$ . The solution separated from the camphoric acid gave the characteristic action of hydroxylamine with Fehling's solution, and showed a strong reducing action on cold ammoniacal silver nitrate.

*Action of Hydroxylamine on Camphoric Anhydride.*

Three oximes derived from camphoric anhydride are possible, corresponding with the formulæ



$\alpha$ -Camphoryl-oxime.

Sym-camphoryl-oxime.

$\kappa$ -Camphoryl-oxime.

3 x 2

where the carbon atoms marked  $\alpha$  and  $\kappa$  are those which in camphor appear in the form of a methylene and a carbonyl group respectively,

as shown by the formula  $\text{C}_8\text{H}_{14} \begin{matrix} \text{CH}_2 & \alpha \\ \diagup & \\ \text{CO} & \kappa \end{matrix}$ . The formation of 'campho-

nitrophenol' by isomeric change from nitrocamphor renders it probable that the isonitroso-group is still combined with the  $\alpha$ -carbon atom, and the third formula is, therefore, not at all probable.

An oxime, corresponding to one of the above formulæ, is already known, namely, that prepared by Errara from hydroxylamine and camphoric anhydride (*Gazzetta*, 1894, 24, ii, 336), and it was, therefore, important to make a detailed comparison of this substance with 'camphonitrophenol,' in order to ascertain whether the synthetical oxime is isomeric or identical with that produced by isomeric change from nitrocamphor; this comparison was all the more necessary in view of the fact that the  $\alpha$ - and  $\kappa$ -camphoryloximes would probably resemble each other closely in many of their properties, and might even occur together in the form of an isomorphous mixture.

According to Errara, the first product of the action of sodium ethoxide (5 mols.) on a solution of camphoric anhydride (3 mols.) and hydroxylamine hydrochloride (3 mols.) in boiling spirit is, a sodium salt of the formula  $\text{C}_{30}\text{H}_{44}\text{N}_2\text{O}_{10}\text{Na}_2$ ; this substance is however, merely a mixture of the sodium salts of camphoryloxime and camphoric acid, as is shown by the following facts.

1.—The free acid does not exist, for when the sodium salt is decomposed by hydrochloric acid, or the lead salt by hydrogen sulphide, the product is merely a mixture of camphoric acid and camphoryloxime (Errara).

2.—On acting on the sodium salt with benzoic chloride in presence of an excess of potash, a benzoate is obtained which melts at  $138^\circ$ , and the specific rotatory power of which is  $[\alpha]_D = +9.1^\circ$  in a 5 per cent. solution in chloroform; it is therefore identical with the benzoate prepared from pure camphoryloxime (see below).

3.—By acting on the sodium salt with acetic anhydride and fused sodium acetate, a mixture of the acetate of camphoryloxime with camphoric anhydride is obtained, from which the latter can be isolated in a pure state by crystallising two or three times from spirit.

4.—By using only one molecular proportion of sodium ethoxide to one of camphoric anhydride and one of hydroxylamine hydrochloride, instead of the excess recommended by Errara, it is, however, possible to avoid the formation of camphoric acid altogether, and thus to obtain a much larger yield of camphoryloxime.

The camphoric anhydride used in the experiments described in the

next paragraph was prepared from camphoric acid by Maissen's method (*Jahresbericht*, 1880, 881) by warming with acetic anhydride and fused sodium acetate; this method gives a very clean product, and is specially well adapted for characterising small quantities of camphoric acid. Camphoric anhydride is usually stated to be optically inactive, but it yields active derivatives, and must, therefore, itself be active to a greater or less degree. I have determined the specific rotatory power of the recrystallised substance in chloroform solution, and have obtained an observed rotation  $\alpha_D = -10'$  for a 10 per cent. solution in a 20 cm. tube, whilst for a 20 per cent. solution  $\alpha_D = -20'$ ; camphoric anhydride is, therefore, a levorotatory substance, its specific rotatory power being  $[\alpha]_D = -0.8^\circ$  in chloroform solution.

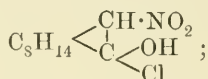
The method which has been adopted in preparing camphoryloxime is as follows: 35 grams of crystallised camphoric anhydride and 7 grams of hydroxylamine hydrochloride are dissolved in a minimum quantity of boiling spirit, and a solution of 5 grams of sodium in absolute alcohol is added gradually. When all the sodium ethoxide has been added, the solution is made distinctly acid with hydrochloric acid, and the greater part of the spirit is distilled off; after filtering off the precipitated sodium chloride, the solution is evaporated down on a water bath and the product dried at  $100^\circ$ . On treating the residue with benzene, the camphoryloxime dissolves; the solution, when evaporated, leaves the oxime in a crystalline form, the yield amounting to about 80 per cent. of the camphoric anhydride used. In order to complete the purification, the substance is first crystallised from water and then dried and crystallised from dry ether, to obtain it in the anhydrous form.

The melting point and specific rotatory power of the purified oxime were accurately determined, as well as those of the benzoate and acetate; as a result, the identity of Errara's camphoryloxime with camphonitrophenol was completely established, as is shown by the following table.

Substance.	Melting point.	$[\alpha]_D$ (chloroform).
Oxime from nitrocamphor.....	$223^\circ \text{ C}$	$+7.0^\circ$
„ „ camphoric anhydride.....	$223 \text{ C}$	$+7.0$
Benzoate from nitrocamphor.....	$138^\circ \text{ C}$	$+9.3^\circ$
„ „ camphoric anhydride.....	$138 \text{ C}$	$+9.3$
Acetate from nitrocamphor.....	$115^\circ \text{ C}$	$+6.8^\circ$
„ „ camphoric anhydride.....	$115 \text{ C}$	$+6.7$

It may also be pointed out that when the crystalline measurements of the two preparations made by Errara and by Morell are expressed in a similar manner, they are substantially identical.

The hydrochloride of nitrocamphor, which appears to be the first product of the action of hydrochloric acid on nitrocamphor, was represented by Cazeneuve by the formula



this formula does not give any adequate representation of the properties of the substance, and it is hoped that further study will afford the data necessary for establishing its constitution. It may, however, be mentioned that a hydrobromide has been prepared from nitrocamphor which behaves in an entirely different manner from the hydrochloride, and appears to possess the properties of an acid bromide.

ERRATUM.—The specific rotatory power of  $\beta\alpha$ -dibromocamphor  $[\alpha]_D = +78^\circ$  represents the value obtained in a solution in benzene, and not in chloroform, as previously stated (this vol., p. 588).

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## XCIX.—*Formation of Ethereal Salts of Polycarboxylic Acids.*

By SIEGFRIED RUHEMANN, Ph.D., M.A., and A. V. CUNNINGTON, B.A.,  
Scholar of Christ's College, Cambridge.

AFTER it had been found by one of us that ethylic aconitate is readily transformed into citrazinamide, and that, in like manner, ethylic glutaconate and its homologues condense with ammonia to form pyridine derivatives, the idea occurred to us to apply this reaction to ethereal salts of unsaturated acids, which stand in a close relation to glutaconic and aconitic acids, with the view of arriving at compounds belonging to the pyridine series. For the synthesis of such ethereal salts, a method was proposed by A. Michael (*J. pr. Chem.*, 1887, [ii], 35, 349), which has since been modified by Auwers and his pupils (*Ber.*, 1891, 24, 307, 2887).

Of these two methods, preference is to be given to that of Michael, a modification of which has been employed in this research, namely,

using sodium ethoxide dried in a vacuum at  $180^{\circ}$ , instead of granulated sodium; the details are given in the experimental section.

In the course of our experiments, we made the interesting observation that a very small quantity of sodium ethoxide is sufficient to effect the union of the ethereal salt of the above acids with that of the unsaturated acid, heat being developed in most cases.

The readiness with which the combination takes place depends, not only on the nature of the ethereal salt of the unsaturated acid, but also on that of the malonic acid (or its homologue), and seems in some measure to be determined by the negative character of both reacting ethereal salts; for as the negative character is diminished by the introduction of an alkyl into ethylic malonate, or into the ethylic salt of the unsaturated acid, so does the development of heat decrease.

Although this difference is very evident, we intend to determine the thermal variation in the heat evolution with the view of establishing fixed values for the influence which groups, entering into these ethereal salts, exert on the course of this reaction.

Some of the compounds described in this paper have been previously obtained by Michael and Auwers, but we thought it advisable to analyse them for the purpose of identification, as the boiling points, in most cases, had been determined at a pressure different from that which we used.

#### EXPERIMENTAL.

*Ethylic propanetetra-carboxylate*,  $\text{COOC}_2\text{H}_5 \cdot \text{CH} < \begin{matrix} \text{CH}(\text{COOC}_2\text{H}_5)_2 \\ \text{CH}_2\text{COOC}_2\text{H}_5 \end{matrix}$ .

The formation of this ethereal salt takes place with the greatest ease.

A mixture of 8 grams of ethylic malonate (1 mol.) and 8.6 grams of ethylic fumarate (1 mol.), on the addition of 0.5 gram of sodium ethoxide, turns yellow and becomes exceedingly hot; the product when cold is acidified with dilute sulphuric acid, the oil extracted with ether, and after removal of the latter distilled under diminished pressure; more than 15 grams of ethylic propanetetra-carboxylate are thus obtained, boiling at  $200^{\circ}$  under a pressure of 14 mm.

The identity of this product with the compound obtained by Michael and Schulthess (*J. pr. Chem.*, 1891, [ii], 45, 56) is sufficiently established by the boiling point, which they gave as  $202\text{--}203^{\circ}$  (pressure 16 mm.).

*Action of Ammonia on Ethylic Propanetetra-carboxylate.*—Concentrated aqueous ammonia acts but slowly on the ethylic salt, the oil not disappearing for a week, part of the product appearing as a crys



talline deposit on the sides of the vessel; this is somewhat soluble in cold water, readily so on boiling, and crystallises from the aqueous solution in colourless prisms which melt with decomposition at 237—238°.

The ammoniacal mother liquor, on concentration, gives a second crop of the same substance, but the whole amount which is formed corresponds with about half only of that required by theory, the remainder being converted into a very soluble ammonium salt.

The composition of the compound, as ascertained by analysis, corresponds with the formula for the diamido-imide of propanetetra-carboxylic acid,  $\text{NH} \begin{matrix} \text{CO} \cdot \text{CH} \cdot \text{CH}_2 \cdot \text{CONH}_2 \\ \text{CO} \cdot \text{CH} \cdot \text{CONH}_2 \end{matrix}$ .

0.2136 gave 0.3268  $\text{CO}_2$  and 0.0904  $\text{H}_2\text{O}$ . C = 41.73; H = 4.70.

0.2192 „ 0.3370  $\text{CO}_2$  „ 0.0890  $\text{H}_2\text{O}$ . C = 41.92; H = 4.61.

0.1800 „ 32 c.c. of nitrogen at 16° and 759 mm. N = 21.07.

$\text{C}_7\text{H}_9\text{N}_3\text{O}_4$  requires C = 42.21; H = 4.52; N = 21.11 per cent.

*Action of Bromine on the Ethylic Salt.*—Bromine acts on the ethereal salt with formation of a substitution product. Although a considerable amount of heat is developed on adding the halogen to the oil, yet the reaction is not complete, a small quantity of the reagents remaining unaltered. As the bromo-derivative suffers decomposition on distillation, we analysed it after it had been freed from the bromine and its hydride by heating at 100° under diminished pressure, and allowed to stand in a vacuum over potash and sulphuric acid until the weight was constant.

The following results were obtained with samples from different preparations.

0.3208 gave 0.1335 AgBr. Br = 17.70.

0.5138 „ 0.2263 AgBr. Br = 18.74.

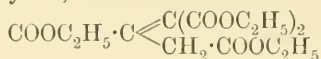
$\text{C}_{15}\text{H}_{23}\text{BrO}_8$  requires Br = 19.46 per cent.

The ethereal salt of the bromo-acid, on heating at 210—215°, loses hydrogen bromide, and the product, when distilled after an hour's exposure to that temperature, yields an oil which boils at 195—204° (pressure 16 mm.), but still contains a small quantity of bromine.

We have made several experiments with the object of obtaining the ethylic salt of propylenetetracarboxylic acid, which appears to be the product formed when the bromo-acid is heated. On redistilling the oil, the amount of bromine is diminished, but its entire removal cannot be accomplished by repeating the operation; it is, however, effected by digesting a solution of the oil in absolute alcohol with small quantities of sodium ethylate until the presence of the halogen can no longer be detected by Beilstein's test.

The compound obtained after this treatment boils at 198--199° (pressure 12 mm.).

The following analytical data indicate that it is almost pure ethylic propylenetetracarboxylate,



0.2348 gave 0.4675 CO<sub>2</sub> and 0.1515 H<sub>2</sub>O. C = 54.30 ; H = 7.16.

C<sub>15</sub>H<sub>22</sub>O<sub>8</sub> requires C = 54.54 ; H = 6.67 per cent.

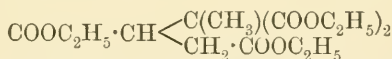
Further experiments with the view of supporting the formula of this product and of transforming it into a pyridine derivative are in progress.

*Ethylic α-Methylpropanetetracarboxylate.*

This ethereal salt has been obtained before by Auwers, Köbner, and v. Meyenburg (*Ber.*, 1891, 24, 2890) by digesting for some hours on the water bath equivalent quantities of ethylic methylmalonate, sodium, and ethylic fumarate in alcoholic solution. They find that the reaction is accompanied by a dark green coloration, and that the oil, which separates on adding water and dilute sulphuric acid, boils at 190--210° under a pressure of 20 mm.; the chief portion at 196--198°.

Using our modified method, the result obtained is as follows. The mixture of ethylic fumarate and ethylic methylmalonate, on the addition of 0.5 gram of sodium ethoxide, becomes yellow and evolves heat, which, however, is much less than in the case of ethylic malonate. The reaction is completed by 2--3 hours digestion on the water bath. The oil, after washing with dilute sulphuric acid, boils at 201° (pressure 12 mm.), only a very small quantity distilling below that temperature ;  $d_{26^\circ/26^\circ} = 1.1153$ .

The analytical numbers correspond with the formula for ethylic methylpropanetetracarboxylate,



0.2445 gave 0.4958 CO<sub>2</sub> and 0.1642 H<sub>2</sub>O. C = 55.30 ; H = 7.46.

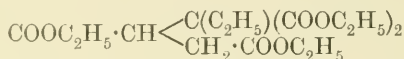
C<sub>16</sub>H<sub>26</sub>O<sub>8</sub> requires C = 55.49 ; H = 7.51 per cent.

*Ethylic Ethylpropanetetracarboxylate.*

The heat which is evolved on the addition of 0.5 gram of sodium ethoxide to the mixture of equivalent quantities of the ethereal salts of ethylmalonic and fumaric acids is very small, and the time of digestion required for the completion of the reaction much longer than in

the former cases. After 4 hours heating on the water bath, only partial combination has taken place, but the fraction of low-boiling point, containing the unaltered ethereal salts, on prolonged warming with a little sodium alcoholate, is also transformed into ethylic ethylpropane-tetracarboxylate, which distils at 203—204° (pressure 11 mm.);  $d_{23^{\circ}/23^{\circ}} = 1.1042$ .

The result of the analysis agrees with the formula



0.2437 gave 0.5015  $\text{CO}_2$  and 0.1705  $\text{H}_2\text{O}$ .  $\text{C} = 56.12$ ;  $\text{H} = 7.77$ .

$\text{C}_{17}\text{H}_{28}\text{O}_8$  requires  $\text{C} = 56.66$ ;  $\text{H} = 7.77$  per cent.

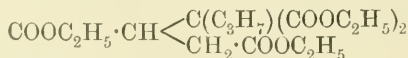
*Ethylic Isopropylpropanetetracarboxylate.*

Auwers and his pupils (*loc. cit.*), who prepared this ethereal salt by the combination of the sodium derivative of ethylic isopropylmalonate and ethylic fumarate, give the boiling point as 205—206° (pressure 19 mm.). They did not, however, analyse the compound.

The union of the two salts takes place readily on treatment by our method, and is almost complete after 3—4 hours warming on the water bath.

The compound boils at 204—205° (pressure 12 mm.), and has the sp. gr.  $d_{27^{\circ}/27^{\circ}} = 1.0964$ .

The formula of the compound



is verified by the following analytical result.

0.2162 gave 0.4545  $\text{CO}_2$  and 0.1550  $\text{H}_2\text{O}$ .  $\text{C} = 57.33$ ;  $\text{H} = 7.96$ .

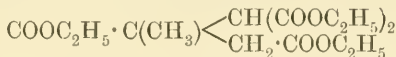
$\text{C}_{18}\text{H}_{30}\text{O}_8$  requires  $\text{C} = 57.75$ ;  $\text{H} = 8.02$  per cent.

*Ethylic  $\beta$ -Methylpropanetetracarboxylate.*

The experiments described above show the influence which the introduction of hydrocarbon groups into the molecule of ethylic malonate has on the interaction of the resulting ethereal salts and ethylic fumarate, and an analogous difference is found when using the ethylic salt of a homologue instead of ethylic fumarate. As ethylic mesaconate was not at our disposal, we took ethylic citraconate. The mixture of the ethylic salts of citraconic and malonic acids, on adding sodium ethoxide, becomes only slightly warm, and several hours digestion on the water bath is necessary to effect their union.

The chief portion of the oily product boils at 200—201° (pressure 12 mm.) and has the density  $d_{25^\circ/25^\circ} = 1.1055$ .

The result of the analysis is in accordance with the formula for ethylic  $\beta$ -methylpropanetetracarboxylate.



0.2368 gave 0.4805  $\text{CO}_2$  and 0.1580  $\text{H}_2\text{O}$ .  $\text{C} = 55.34$ ;  $\text{H} = 7.41$ .

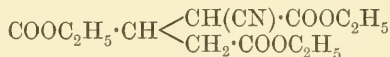
$\text{C}_{16}\text{H}_{26}\text{O}_8$  requires  $\text{C} = 55.49$ ;  $\text{H} = 7.51$  per cent.

This ethereal salt also had been prepared before by Michael and Schulthess (*loc. cit.*) and by Anwers (*Ber.*, 1891, 24, 2894) by heating on the water bath a mixture of ethylic malonate and ethylic citraconate with an alcoholic solution of sodium ethoxide.

#### *Ethylic Cyanotricarballylate.*

Ethylic cyanacetate (4.3 grams) reacts with ethylic fumarate (4.8 grams) in the presence of sodium ethoxide (0.5 gram) with great evolution of heat; after one hour's subsequent digestion on the water bath, the union is complete. The product, on treatment with dilute sulphuric acid, extraction with ether, &c., and two rectifications, yields a pale yellow oil (about 6 grams) which boils at 197—199° (pressure 11 mm.);  $d_{26^\circ/26^\circ} = 1.1257$ .

On analysis, the following numbers were obtained, which correspond with the formula



0.2588 gave 0.5205  $\text{CO}_2$  and 0.1605  $\text{H}_2\text{O}$ .  $\text{C} = 54.85$ ;  $\text{H} = 6.88$ .

$\text{C}_{13}\text{H}_{19}\text{NO}_6$  requires  $\text{C} = 54.73$ ;  $\text{H} = 6.67$  per cent.

Müller (*Compt. rend.*, 1892, 114, 1204), who obtained this ethereal salt by heating a mixture of ethylic cyanacetate and ethylic fumarate with an alcoholic solution of sodium ethoxide, found that it boiled at 180—190° under a pressure of 15—20 mm.

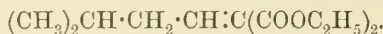
#### *Ethylic iso-Amylidenedimalonate.*

The action of ethylic malonate on ethylic iso-amylidenemalonate in the presence of sodium ethoxide is quite in accordance with the view expressed before as to the influence which the negative character of the ethereal salts has on their power of combining.

*Ethylic isoamylidenemalonate* was prepared by the method Komnenos (*Annalen*, 218, 107) used for obtaining ethylic ethylidenemalonate, namely, by heating a mixture of ethylic malate

(32 grams), acetic anhydride (32 grams), and valeraldehyde (25 grams) at 100° in a soda-water bottle for 3—4 days. The liquid is then distilled, at the ordinary pressure, to remove unaltered aldehyde and acetic anhydride, and the oily residue fractionated under diminished pressure. After repeated rectifications, the ethereal salt is obtained as a colourless oil which has an odour of valeraldehyde, and boils at 133—135° (11 mm.).

The following analytical results correspond with the formula



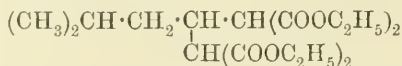
0.2168 gave 0.5034  $\text{CO}_2$  and 0.1718  $\text{H}_2\text{O}$ .  $\text{C} = 63.32$ ;  $\text{H} = 8.80$ .

$\text{C}_{12}\text{H}_{20}\text{O}_4$  requires  $\text{C} = 63.15$ ;  $\text{H} = 8.77$  per cent.

The yield is unsatisfactory, as from the above quantities only 13.5 grams of the ethereal salt were obtained, a large portion of the reagents remaining unaltered, even on heating the mixture at 150° for 8—10 hours.

On the addition of 0.5 gram of sodium ethoxide to the mixture of 8 grams of ethylic iso-amyliidenemalonate and 5.7 grams of ethylic malonate, a strong development of heat takes place; after being allowed to stand for an hour, the compound is isolated as in the former cases. The pale yellow oil obtained after two rectifications amounts to about 9 grams, and boils at 208—209° (at 12 mm.);  $d_{27^\circ/27^\circ} = 1.0645$ .

The result of the analysis agrees with the formula for ethylic iso-amylienedimalonate,



0.2482 gave 0.5375  $\text{CO}_2$  and 0.1840  $\text{H}_2\text{O}$ .  $\text{C} = 59.0$ ;  $\text{H} = 8.23$ .

$\text{C}_{19}\text{H}_{32}\text{O}_8$  requires  $\text{C} = 58.76$ ;  $\text{H} = 8.22$  per cent.

### *Ethylic Propanepentacarboxylate.*

Bishop and Perkin (Proc. Chem. Soc., 1891, 41) some years ago, by the interaction of ethylic dichloracetate and ethylic monosodiummalonate, obtained the ethereal salts of ethylenetricarboxylic acid,  $(\text{COOC}_2\text{H}_5)_2\text{C}\cdot\text{CH}\cdot\text{COOC}_2\text{H}_5$ , and of propanepentacarboxylic acid,  $(\text{COOC}_2\text{H}_5)_2\text{CH}\cdot\text{CH}(\text{COOC}_2\text{H}_5)\cdot\text{CH}(\text{COOC}_2\text{H}_5)_2$ .

We have repeated their experiment with the object of ascertaining whether the ethylic salt of the unsaturated acid, in the presence of sodium ethoxide, condenses with ethylic malonate to form ethylic propanepentacarboxylate.

The action of ethylic dichloracetate on ethylic malonate and sodium



ethoxide in alcoholic solution takes place very slowly, and is not complete, even on heating the mixture at  $100^{\circ}$ . The product, after removal of the alcohol, is mixed with water, extracted with ether, &c., and fractionally distilled several times before fractions can be obtained of constant boiling point. One of these, ethylic ethylenetricarboxylate, is a colourless oil which distils at  $158^{\circ}$  (pressure 12 mm.), and has the density  $d_{27^{\circ}/27^{\circ}} = 1.0888$ . Bishop and Perkin found that it boiled at  $203\text{--}205^{\circ}$  (pressure 100 mm.).

The analytical results correspond with the formula given above.

0.2187 gave 0.4315  $\text{CO}_2$  and 0.1360  $\text{H}_2\text{O}$ .  $\text{C} = 53.81$ ;  $\text{H} = 6.90$ .

$\text{C}_{11}\text{H}_{16}\text{O}_6$  requires  $\text{C} = 54.09$ ;  $\text{H} = 6.56$  per cent.

The fraction of higher boiling point obtained in the above reaction, after repeated fractionations, yields a viscid oil which distils at  $223\text{--}225^{\circ}$  under a pressure of 10 mm.;  $d_{27^{\circ}/27^{\circ}} = 1.1418$ . (Bishop and Perkin observed the boiling point to be  $265^{\circ}$  at a pressure of 80 mm.)

The following analytical data correspond with the formula for ethylic propanepentacarboxylate.

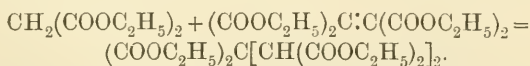
0.2258 gave 0.4445  $\text{CO}_2$  and 0.1450  $\text{H}_2\text{O}$ .  $\text{C} = 53.68$ ;  $\text{H} = 7.13$ .

$\text{C}_{18}\text{H}_{28}\text{O}_{10}$  requires  $\text{C} = 53.46$ ;  $\text{H} = 6.93$  per cent.

This ethereal salt can also be obtained from ethylic ethylenetricarboxylate by mixing the latter with the equivalent quantity of ethylic malonate and a little sodium ethoxide, the reaction being accompanied by a marked evolution of heat. The identity of the compound thus formed and ethylic propanepentacarboxylate was proved by its boiling point.

#### *Ethylic Propanehexacarboxylate.*

A further support for the view as to the influence of the negative character of the ethereal salts on the course of the reaction is afforded by the behaviour of ethylic malonate towards ethylic ethylenetetracarboxylate (ethylic dicarbintetracarboxylate) in the presence of sodium ethoxide. The mixture becomes very hot, and the action is complete after 1 hour's digestion on the water bath, ethylic propanehexacarboxylate being formed.



The compound distils at  $246^{\circ}$  under a pressure of 15 mm., and is a very viscous, yellow oil.

On analysis, the following numbers were obtained.

0.2410 gave 0.4675  $\text{CO}_2$  and 0.1480  $\text{H}_2\text{O}$ .  $\text{C} = 52.90$  ;  $\text{H} = 6.82$ .

$\text{C}_{21}\text{H}_{32}\text{O}_{12}$  requires  $\text{C} = 52.94$  ;  $\text{H} = 6.72$  per cent.

*Ethylic Butanepentacarboxylate.*

Auwers (*Ber.*, 1893, 26, 364), on examining the product formed by digesting a mixture of ethylic malonate and the ethereal salt of an unsaturated acid with sodium ethoxide dissolved in alcohol, was led to the conclusion that, on using the ethylic salts of unsaturated dicarboxylic acids, the reaction proceeded in one direction only, but that it was complicated when salts of unsaturated tricarboxylic acids were used. He studied especially the interaction of ethylic sodiomalonate and ethylic aconitate, and from the product of their condensation succeeded in isolating three acids, one of which was butanetetracarboxylic acid,  $\text{CH}_2(\text{COOH}) \cdot \text{CH}(\text{COOH}) \cdot \text{CH}(\text{COOH}) \cdot \text{CH}_2 \cdot \text{COOH}$ . That other acids are produced besides this is undoubtedly due to the fact that ethylic aconitate itself is readily acted on by sodium alcoholate; indeed, on adding a trace of sodium alcoholate in the dry state or in alcoholic solution to the ethereal salt, a deep red coloration is produced, and on treating this red liquid with an acid, the colour disappears and an oil is obtained which decomposes on distillation under diminished pressure; the results of the investigation of this reaction will be published at some future date. This serves to explain Auwers' observation.

On applying our method, however, we find that the interaction of ethylic aconitate and ethylic malonate takes place with the formation of one product only, namely, ethylic butanepentacarboxylate; the mixture becomes warm and acquires a yellow colour; after standing at the temperature of the room for  $1\frac{1}{2}$  hours, about half the quantity of the ethereal salts has entered into combination. The yield of ethylic butanepentacarboxylate is very satisfactory (more than 80 per cent. of the theoretical) if the mixture is heated on the water bath for a few hours. The product is a slightly yellowish oil which boils without decomposition at  $232-233^\circ$  (pressure 12 mm.);  $d_{21^\circ/21^\circ} = 1.0660$ .

The analytical values correspond with the formula given above.

0.2685 gave 0.5362  $\text{CO}_2$  and 0.1730  $\text{H}_2\text{O}$ .  $\text{C} = 54.46$  ;  $\text{H} = 7.16$ .

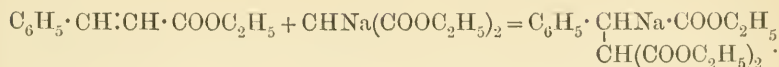
$\text{C}_{19}\text{H}_{30}\text{O}_{10}$  requires  $\text{C} = 54.54$  ;  $\text{H} = 7.17$  per cent.

*Ethylic Phenylpropanetricarboxylate.*

The sodium derivative of this ethereal salt is the product which is formed by the union of ethylic sodiomalonate and ethylic cinnamate.

According to Michael's "positive-negative" theory of addition, this

combination takes place in the manner indicated by the following equation,



The combination, as Michael (*J. pr. Chem.*, 1887, [ii], 35, 351) found, is effected on keeping the mixture of the two compounds, in absolute alcohol, for several days.

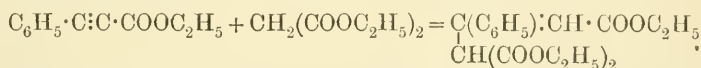
The action of sodium ethoxide (0.5 gram) on a mixture of the ethylic salts of malonic and cinnamic acids, we find, differs most markedly from the action which takes place in the cases recorded above, as no evolution of heat is noticeable.

Combination takes place very slowly, even at 100°, with formation of ethylic phenylpropanetricarboxylate, which is characterised as such by the boiling point, which was observed to be 216° (pressure 14 mm.), whilst Michael gives it as 213—215° (pressure 15 mm.).

#### *Ethylic Phenylpropylenetricarboxylate.*

Ethylic sodiomalonate, as shown by Michael (*J. pr. Chem.*, 1894, [ii], 49, 20) combines with the ethereal salts of acids belonging to the acetylene series, and this reaction gives rise to ethereal salts of unsaturated polycarboxylic acids.

On using, for instance, ethylic phenylpropionate, ethylic phenylpropylenetricarboxylate is formed, according to the equation,



The combination of these ethereal salts, in working according to Michael's directions, takes place rather slowly, whilst we find that it is readily effected by the addition of a small quantity of sodium ethoxide. The reaction, which is accompanied by evolution of heat, is aided by subsequent warming on the water bath for 3—4 hours. The dark red oil, thus obtained, is mixed with dilute sulphuric acid, extracted with ether, &c., and distilled under diminished pressure. The distillation is accompanied by partial decomposition, as was observed by Michael, but the yellow oil which passes over between 215° and 220°, at a pressure of about 11 mm.,  $d_{27^\circ/27^\circ} = 1.1232$ , is sufficiently pure, as indicated by the following analysis.

0.2145 gave 0.5100 CO<sub>2</sub> and 0.1295 H<sub>2</sub>O. C = 64.89 ; H = 6.70.

C<sub>18</sub>H<sub>22</sub>O<sub>6</sub> requires C = 64.67 ; H = 6.58 per cent.

The ethereal salts of unsaturated acids, which are thus formed, will be isomeric with those which result from the removal of hydrogen

bromide from the bromo-substitution products of the corresponding salts of the saturated series of acids.

Their further study, with the object of transforming them into pyridine derivatives, will form the subject of a future communication.

GONVILLE AND CAIUS COLLEGE,  
CAMBRIDGE.

C.—*Yellow Colouring Principles contained in Various Tannin Matters. Part VI. Rhus Cotinus and Rhus Rhodanthema.*

By ARTHUR GEORGE PERKIN, F.R.S.E.

As in a previous investigation (Trans., 1896, 69, 1299) the colouring of Sicilian sumach, *R. Coriaria*, was found to be myricetin, and not quercetin as stated by Löwe (*Zeit. anal. Chem.*, 1874, 12, 127), it seemed desirable to re-examine the Venetian variety, *R. Cotinus*, in which he had also detected the presence of quercetin. As is well known, the wood of this tree, young fustic, contains fisetin, and consequently it would be particularly interesting to ascertain whether quercetin, a more highly oxidised colouring matter of the same group, existed in the leaves. Considerable difficulty was experienced in obtaining a Venetian sumach of trustworthy origin, as this, like the Sicilian variety, is often adulterated; a commercial sample in the form of powder, for which I am indebted to the kindness of Mr. A. Gilardini, of Turin, was examined (Trans., 1897, 71, 1136), but the results were considered untrustworthy, the material being evidently impure. Eventually, I was successful in obtaining an introduction to Messrs. Dammann and Co., San Giovanni, near Naples, who were good enough to send me leaves specially plucked from trees growing on their own farm.

The ground leaves were extracted with 10 times their weight of boiling water, filtered through calico, and the filtrate, while hot, treated with lead acetate solution as long as a precipitate was formed; this was collected, decomposed with boiling dilute sulphuric acid, the lead sulphate removed, the clear liquid extracted with ether, and the ether evaporated, when a crystalline residue was left; this, on being treated with water, deposited a yellow, flocculent precipitate of the colouring matter, which, after being washed with water and with chloroform, was purified by crystallisation from dilute alcohol.

0.1086 gave 0.2237 CO<sub>2</sub> and 0.0347 H<sub>2</sub>O. C = 56.18; H = 3.54.

C<sub>15</sub>H<sub>10</sub>O<sub>8</sub> requires C = 56.60; H = 3.14 per cent.

It forms a glistening mass of pale yellow needles, which in alcoholic solution gave, with lead acetate, an orange-red precipitate, and with ferric chloride a brownish-black coloration. Dilute alkalis dissolved it with a deep green tint.

The acetyl derivative crystallised from alcohol in colourless needles melting at 204—206°.

0.1080 gave 0.2240 CO<sub>2</sub> and 0.0390 H<sub>2</sub>O. C = 56.57 ; H = 4.01.

C<sub>15</sub>H<sub>4</sub>O<sub>8</sub>(C<sub>2</sub>H<sub>3</sub>O)<sub>6</sub> requires C = 56.84 ; H = 3.86 per cent.

Fusion with alkali gave phloroglucinol, and gallic acid crystallising in colourless needles which melted at 236—237°. The colouring matter of Venetian sumach (*R. Cotinus*) is therefore *myricetin*, and Löwe's statement that it contains quercetin is incorrect. The yield of myricetin from the leaves is approximately 0.1 per cent.

*Tanning Properties.*—As no record of the tanning-properties of these leaves could be found, it appeared desirable, while in possession of a pure sample, to submit them to examination. Professor Procter was good enough to undertake this, and I am indebted to him for the following account of his results:

Tanning matter .....	16.7	per cent.
Soluble non-tannins .....	14.4	„
Insoluble at 60° F. per cent....	57.5	„
Water .....	11.4	„
	<hr/> 100.0	„

It gives a light-coloured leather, although slightly darker than that produced by *R. Coriaria*, the tannin content of the latter (about 21 per cent.) is, however, greater. According to Watt (*Dict. of Econ. Products of India*, vol. vi., p. 495), an unlimited supply of this material exists in India, on the lower Himalaya, it is, however, but little used except by native tanners. It is difficult to understand why no greater outlet is found for so valuable a material, unless the Indian product, through circumstances of climate and cultivation, is of much poorer quality than the above.

### *Rhus Rhodanthema.*

The results of the examination of the wood of this tree (Trans., 1897, '71, 1194) showed that, like *R. Cotinus*, it contained fisetin, although, on the other hand, the glucoside present was not identical with Schmid's fustin (*Ber.*, 1886, 19, 1735). Of the numerous species of *Rhus* examined up to the present, only *R. Cotinus* and *R. rhodanthema* are known to contain colouring matter in the stem, although from the



description given it seems probable that the Indian varieties, *R. insignis*, *mysorensis*, *parviflora*, and *wallachi* (*Watt's Dict. Economic Products of India*, vol. vi., p. 496) resemble them in this respect. A comparison of the New South Wales and Venetian sumachs was therefore interesting, to determine if in the former case the leaves also contain a colouring matter distinct from that occurring in the stem. For the material employed, I am indebted to the kindness of Mr. H. G. Smith, of the Botanical Museum, Sydney. It has not been previously examined. When digested with boiling water, the ground leaves emitted a pungent odour resembling that of eucalyptus oil, and the hot mixture filtered so imperfectly that it was necessary to squeeze it through calico and remove the final traces of extract by strong pressure. From the hot, opaque filtrate, the colouring matter was isolated by the method employed with *R. Cotinus*, and the yellow, flocculent product purified by crystallisation from dilute alcohol.

0.1050 gave 0.2306  $\text{CO}_2$  and 0.0368  $\text{H}_2\text{O}$ . C = 59.89 ; H = 3.89.

$\text{C}_{15}\text{H}_{10}\text{O}_7$  requires C = 59.60 ; H = 3.31 per cent.

It consisted of glistening, yellow needles, soluble in dilute alkalis with a yellow coloration, and giving, with alcoholic lead acetate, an orange-red precipitate. The yield obtained was 0.05 per cent. The *acetyl derivative* formed colourless needles melting at 189—191°.

0.1127 gave 0.2416  $\text{CO}_2$  and 0.0420  $\text{H}_2\text{O}$ . C = 58.46 ; H = 4.14.

$\text{C}_{15}\text{H}_5\text{O}_7(\text{C}_2\text{H}_5\text{O})_5$  requires C = 58.59 ; H = 3.90 per cent.

As by fusion with alkali phloroglucinol and protocathechuic acid were obtained, no doubt could exist that this colouring matter was *quercetin*.

The aqueous filtrate from the crude colouring matter contained a considerable quantity of gallic acid, and this, together with the fact that the leaves dye iron mordanted fabrics a blue-black, indicates the presence of *gallotannic acid*.\*

*Tanning properties*.—These were examined by Prof. Procter at the request of Mr. H. G. Smith, with the object of ascertaining their commercial value.

Tanning matter .....	9.5 per cent.
Soluble non-tannins .....	9.1 „
Insoluble at 60° F. ....	71.0 „
Water .....	10.4 „
	<hr/>
	100.0 „

\* Apparently gallotannic acid exists in the leaves of all species of *Rhus*, for the late Prof. Henry Trimble has isolated this substance from a great number of varieties (private communication).

Leather tanned by these leaves has a considerably darker and redder colour than that produced by the *R. Coriaria* or *R. Cotinus*, and obviously a much larger quantity is necessary to obtain the same tanning effect. From this, it will be seen that they cannot be utilised other than locally.

The above results show that the leaves of *R. Cotinus* and *R. rhodanthema* contain respectively myricetin and quercetin, although in each case the yellow colouring matter of the stem is fisetin. That the leaves of these plants should contain colouring matters which belong probably to the same group as fisetin, and differing from it only in the possession of more hydroxyls, is not only botanically interesting, but suggests a source of colouring matters which may possess much scientific interest. The results in this direction, however, have hitherto been disappointing, for the leaves of *Artocarpus integrifolia*, the wood of which contains morin and cyanomac lurin (Trans., 1895, 97, 937); *A. incisa*,\* the bread fruit tree; and *A. lakoocha*, procured through the kindness of Mr. J. Ingelby, of Leeds, were either devoid of or contained such minute traces of colouring principles that it was hopeless to attempt their further examination. On the other hand, the leaves of the logwood tree (*Hæmatoxylon campechianum*) of old fustic (*Morus tinctoria*), the madder plant, and *Polygonum cuspidatum* contain sufficient colouring matter for investigation, and efforts are being made to procure these and the leaves of other well-known dye-stuffs, with the hope that they may give interesting results.

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## CI.—Colouring Matters of the New Zealand Dyewood *Puriri, Vitex littoralis.* Part I.

By ARTHUR GEORGE PERKIN, F.R.S.E.

My attention was first directed to this yellow dye-stuff by Sir Thomas Wardle, who, on behalf of Mr. A. G. Purchas, of Epsom, Auckland, forwarded me about two years ago a small sample for an opinion as to its commercial value. The experiments then made indicated that it possessed but half the strength of quercitron bark or old fustic, moreover, its dyeing properties were somewhat peculiar and suggested

\* The wood of this tree is also devoid of colouring matter.

the presence of a new colouring matter. With the object of ascertaining if this was the case, and a desire to be quite certain of the commercial utility or otherwise of this material, application was made to Mr. Purchas for a larger supply, and my thanks are due to him for the very cordial and liberal manner in which he acceded to my request. To him, and also the authorities of the Royal Gardens, Kew, I am indebted for the following account of this plant.

The *Vitex littoralis* or "Puviri" is a large tree, forty to sixty feet high and three to five feet in diameter, which grows only in the northern portion of the North Island of New Zealand, where it has been somewhat ruthlessly destroyed by the settlers. The wood affords a very durable timber, which takes a fine polish, but is chiefly used for house blocks, fencing posts, piles for bridges, railway sleepers, &c. When growing, it is the natural food of the larvæ of a beautiful green moth (the Puriri moth) which excavates large and long channels though the solid timber, but which does not in any way cause it to rot, and does not attack it in the worked up condition. It varies in colour, the heart wood being brown, and the sap wood yellow. Although Mr. Purchas states that all portions of the tree contain more or less colouring matter, its properties as a dye-stuff appear to be little known.

I am indebted to Messrs. James Richardson and Co., of Leeds, for their kindness in grinding the wood, for its hard, solid nature did not permit of its reduction in the laboratory to a condition suitable for extraction.

#### EXPERIMENTAL.

The finely ground wood, in portions of 1 kilo. at a time, was boiled with 10 times its weight of water for 8 hours, the insoluble residue being collected, washed with water, and well pressed, and one extraction was usually sufficient owing to the readily soluble nature of the colouring matter. The light brown extract, on evaporation, became much darker, and an almost black, treacly residue was left; this was digested with alcohol, filtered from a brown, tarry product devoid of tinctorial property, and the orange-brown filtrate evaporated to dryness, when a dull, orange-coloured, transparent, vitreous residue was left. As experiment showed that the colouring matter was here present as a glucoside, it was decomposed in the following manner.

To 750 c.c. of an aqueous solution of the substance, 30 c.c. of hydrochloric acid was added, and the mixture boiled in a porcelain dish with continued stirring; the liquid rapidly became red, and a black, tarry mass gradually separated accompanied by the evolution of a somewhat acrid vapour; finally, a viscous, yellow product was deposited. After standing 12 hours, the acid liquid was removed by decantation,

the semi-solid mass repeatedly washed by agitation with water, well drained, and digested with boiling alcohol, when a pale yellow, crystalline powder was left; this was collected, washed with boiling alcohol until the filtrate was colourless, the filtrate and washings, *A*, being reserved for examination. In the earlier experiments, this substance was purified by crystallisation from a very large bulk of alcohol, but it soon became evident from its very sparing solubility in this, and in fact all solvents, that such a method was only practicable for very small quantities of material; a better way consisted in acidifying a boiling alkaline solution diluted with its own bulk of alcohol, collecting the crystalline deposit while hot, and washing it with boiling alcohol and acetic acid. The method eventually adopted was, however, to prepare the pure acetyl derivative and reconvert this into the colouring matter in the usual manner. Unfortunately, as is often the case, some loss was here experienced by the formation of secondary products during the acetylation. The yield was approximately 2 per cent. Of the subjoined analyses, 1 and 2 represent the colouring matter crystallised from alcohol, and 3 that regenerated from the acetyl derivative.

0.1076 gave 0.2307  $\text{CO}_2$  and 0.0455  $\text{H}_2\text{O}$ .  $\text{C} = 58.47$ ;  $\text{H} = 4.69$ .

0.1154 „ 0.2481  $\text{CO}_2$  „ 0.0490  $\text{H}_2\text{O}$ .  $\text{C} = 58.63$ ;  $\text{H} = 4.71$ .

0.1237 „ 0.2662  $\text{CO}_2$  „ 0.0510  $\text{H}_2\text{O}$ .  $\text{C} = 58.69$ ;  $\text{H} = 4.58$ .

$\text{C}_{15}\text{H}_{14}\text{O}_7$  requires  $\text{C} = 58.82$ ;  $\text{H} = 4.57$  per cent.

$\text{C}_{17}\text{H}_{16}\text{O}_8$  „  $\text{C} = 58.62$ ;  $\text{H} = 4.59$  „

*Vitexin*, the name proposed for this colouring matter, is a bright, canary-yellow, crystalline powder consisting of minute prismatic or fine hair-like needles, according to the process adopted for its purification. It is very sparingly soluble in alcohol, acetone, acetic acid, water, and nitrobenzene, insoluble in ether and benzene, differing considerably in this respect from the known natural yellow mordant dye-stuffs. So marked is this, that it at first seemed probable that this was not the original colouring matter of the wood, but an anhydride or analogous compound formed during the decomposition of the glucoside with hot acid. Experiments, however, on the action of acid on a solution of the glucoside in the cold, complete after about three weeks, gave the same product, although freer from the tarry impurities formed to such a large extent by the action of the hot acid; in fact, if time were not an object, the cold process is to be recommended, as the subsequent purification is considerably facilitated.

Dilute solutions of the alkalis, alkali carbonates, and ammonia dissolve vitexin with a very pale yellow coloration, and it is deposited in a crystalline condition from the boiling solutions on acidification. When added to boiling alcoholic potash or soda, it is not dissolved, but

acquires a more orange tint, due to the formation of an insoluble compound with the alkali; these products when collected, washed with alcohol, and dried, form canary-coloured, hygroscopic powders readily soluble in water. With the hope of determining the true molecular weight of vitexin, numerous analyses of these compounds were made; unfortunately, however, no concordant results could be obtained, due, on the one hand, to incomplete washing, as the precipitate clotted and became sticky on the filter, and, on the other, to the frequent presence of traces of unattacked substance. Vitexin is readily decomposed by sodium amalgam in the presence of water, yielding a brown solution, which, on neutralisation, develops a beautiful scarlet tint, but no precipitate is formed. With sulphuric acid, it gives a pale yellow solution in the cold, which, on gentle heating, becomes browner, and at about  $170^{\circ}$  acquires an olive-green tint; on pouring into water, no precipitate is formed, and the solution appears to contain the sulphonic acid of some decomposition product. It does not react with mineral acids in the presence of acetic acid, or decompose the alkali acetates in alcoholic solution. In aqueous or alcoholic solution, a trace of ferric chloride yields a reddish-brown coloration, which is changed by excess of the reagent to a brownish-green tint.

*Acetylvitexin*.—Finely powdered vitexin, in small portions at a time, is added to 10 times its weight of boiling acetic anhydride, without the addition of sodium acetate, the presence of which is not beneficial; a clear solution is but slowly formed, and this is boiled for 6 hours. On cooling, the addition of alcohol causes the separation of crystals, which are collected and crystallised from a mixture of acetic acid and alcohol.

0.1222 gave 0.2577  $\text{CO}_2$  and 0.0530  $\text{H}_2\text{O}$ .  $\text{C} = 57.51$ ;  $\text{H} = 4.80$ .

$\text{C}_{15}\text{H}_9\text{O}_7(\text{C}_2\text{H}_3\text{O})_5$  requires  $\text{C} = 58.13$ ;  $\text{H} = 4.65$  per cent.

$\text{C}_{17}\text{H}_{10}\text{O}_8(\text{C}_2\text{H}_3\text{O})_6$  „  $\text{C} = 58.00$ ;  $\text{H} = 4.66$  „

It crystallises in hard, colourless, prismatic needles melting at  $251\text{--}256^{\circ}$ , readily soluble in acetic acid, almost insoluble in alcohol. To determine the acetyl groups present, a solution of the substance in acetic acid was treated with sulphuric acid, and the crystals of the colouring matter which separated on dilution with water collected and weighed.

1.3695 gave 0.7860 colouring matter. Found 57.39.

4.5238 „ 2.5878 „ „ „ 57.20.

$\text{C}_{15}\text{H}_9\text{O}_7(\text{C}_2\text{H}_3\text{O})_5$  requires  $\text{C}_{15}\text{H}_{14}\text{O}_7 = 59.30$  per cent.

$\text{C}_{17}\text{H}_{10}\text{O}_8(\text{C}_2\text{H}_3\text{O})_6$  „  $\text{C}_{17}\text{H}_{16}\text{O}_8 = 58.00$  „

An analysis of the regenerated vitexin has been previously given.

These determinations indicate that of the two formulæ for vitexin,



$C_{17}H_{16}O_8$  is the one which should be adopted, especially as in the above experiments a considerable quantity of material was employed. Unfortunately, owing to the very insoluble nature of this colouring matter, it is impossible to determine its molecular weight by the ordinary methods, and attempts in other directions, such as the preparation of its bromine and azobenzene derivatives in a pure condition, have hitherto been unsuccessful. With bromine in acetic acid, it yields an extremely soluble, colourless compound, and with diazobenzene a reddish-brown precipitate of a resinous nature.

It appeared probable, from the very high percentage of hydrogen and oxygen this substance contains, that it might be the very stable glucoside of a colouring matter, somewhat analogous to fustin, the glucoside of fisetin which occurs in *Rhus Cotinus*. Experiments, however, did not corroborate this view, for vitexin is not changed by long digestion with dilute acids.

#### *Decomposition Products of Vitexin.*

*Action of Fused Alkali.*—The colouring matter was digested with 10 times its weight of caustic potash and a little water at  $190-210^\circ$  for half an hour, and the brown melt dissolved in water and neutralised with acid. The liquid, which had the pungent odour of acetic acid, was extracted with ether and the extract evaporated. The crystalline residue was dissolved in dilute sodium hydrogen carbonate solution, extracted with ether (*B*), and the aqueous liquid neutralised with acid and extracted with ether (*C*).

From extract *B*, *phloroglucinol* was isolated in colourless needles melting at  $208-210^\circ$ .

Extract *C* yielded a crystalline acid, identified as *parahydroxybenzoic acid*; this melted at  $210^\circ$  and gave a brown coloration with aqueous ferric chloride.

0.0912 gave 0.2046  $CO_2$  and 0.0374  $H_2O$ .  $C = 61.18$ ;  $H = 4.55$ .

$C_7H_6O_3$  requires  $C = 60.87$ ;  $H = 4.35$  per cent.

*Action of Potassium Hydroxide Solution* (sp. gr. 1.54).—With the hope of effecting a more limited decomposition of the colouring matter, it was boiled in alkali of the above strength; the yellow liquid gradually assumed a brown tint, and in about half an hour the action was complete. It was then acidified, extracted with ether, and the extract evaporated, leaving a brownish, oily residue which became crystalline after a few hours. This consisted of two substances readily separated by treatment with boiling benzene, in which one of them was nearly insoluble; this was found to be *phloroglucinol*, which after purification was obtained as colourless needles melting at  $210^\circ$ . The benzene

extracts, when concentrated, gradually deposited dark coloured leaflets, which were collected and again crystallised from this solvent. The product was dissolved in boiling water, filtered from a trace of oily matter, and the crystals which separated on cooling finally purified by crystallisation from benzene.

0.1166 gave 0.3033  $\text{CO}_2$  and 0.0635  $\text{H}_2\text{O}$ .  $\text{C} = 70.93$ ;  $\text{H} = 6.05$ .

$\text{C}_8\text{H}_8\text{O}_2$  requires  $\text{C} = 70.59$ ;  $\text{H} = 5.88$  per cent.

It was obtained as colourless needles insoluble in sodium hydrogen carbonate solution, which melted at  $107-108^\circ$ , and gave a faint violet coloration with aqueous ferric chloride. When fused with alkali, it gives parahydroxybenzoic acid and a trace of phenol; it also forms a semicarbazide which crystallises in needles melting at  $196-198^\circ$ . It is, therefore, evidently *parahydroxyacetophenone*, and this was further corroborated by comparing it with a sample of the substance prepared from apigenin in a similar way (Trans., 1897, 71, 805).

When air was aspirated through an alkaline solution of vitexin, it remained unchanged even after 24 hours treatment, and could be recovered almost intact by acidifying the liquid.

*Action of Alcoholic Potash.*—The behaviour of the colouring matter towards this reagent was studied by boiling the mixture for 8 hours, and by heating it in sealed tubes at  $160-170^\circ$  for 4 hours. In each case, it was completely decomposed with formation of phloroglucinol, parahydroxyacetophenone, and parahydroxybenzoic acid; these were isolated and identified by the methods previously described.

*Action of Nitric Acid.*—Vitexin is readily dissolved by cold nitric acid (sp. gr. 1.54), or a mixture of this with an equal volume of sulphuric acid, without any violent action; the solution, on standing, if fairly concentrated, becomes semi-solid after a time, from separation of a light coloured, somewhat gelatinous precipitate. Attempts to collect this, apparently a nitro-derivative of the colouring matter, failed, owing to its solubility in water, especially in the absence of acid; thus, if the acid product was poured into water, a pale yellow precipitate was deposited, which, when collected and washed with water, almost entirely dissolved before the final traces of acid could be removed.

The action of dilute nitric acid, 100 c.c. (15 per cent.), on the colouring matter (4 grams) was now studied; on boiling for half an hour, it dissolved, forming a clear yellow solution, which became turbid on cooling, but if the action was allowed to proceed, a pale yellow, crystalline powder separated in small quantity. This was collected (*D*) and the filtrate evaporated to a small bulk and cooled, when a considerable quantity of colourless crystals separated; these, after draining with the aid of the pump and washing with a little

water, were dried, and the product extracted with boiling benzene, finally crystallising from dilute alcohol.

0.1063 gave 12 c.c. of nitrogen at 25° and 755 mm.  $N = 12.49$ .

0.1065 „ 12.3 „ „ 25° „ 755 mm.  $N = 12.79$ .

$\text{OH} \cdot \text{C}_6\text{H}_2(\text{NO}_2)_2 \cdot \text{COOH}$  requires  $N = 12.28$  per cent.

It crystallised in colourless leaflets melting at 235—237°, sparingly soluble in boiling water, and yielding with alcoholic potash a scarlet potassium salt.

To prepare its ethylic salt, it was treated with an alcoholic solution of hydrogen chloride in the usual manner. The product crystallises in colourless, hair-like needles readily soluble in alcohol and melting at 88—89°.

0.1131 gave 11 c.c. of nitrogen at 22° and 760 mm.  $N = 11.01$ .

$\text{OH} \cdot \text{C}_6\text{H}_2(\text{NO}_2)_2 \cdot \text{COOC}_2\text{H}_5$  requires  $N = 10.93$  per cent.

It is, therefore, dinitroparahydroxybenzoic acid, which has been previously prepared by Salkowski (*Annalen*, 1872, 163, 36) by passing nitrous acid into a solution of dinitroparamidobenzoic acid. Curiously enough, it is described by him as bright yellow, or bright bronze-coloured tables, but this is incorrect, for I have prepared it by the nitration of parahydroxybenzoic acid itself, and the product was colourless and identical in appearance with that obtained above.

The benzene extracts resulting from the purification of the above acid deposited a very small quantity of colourless crystals, consisting mainly of *picric acid*.

The yellow, crystalline powder *D* (see above), of which but 0.2 gram was formed in each operation, was dissolved in boiling nitrobenzene, and the solution cautiously treated with a little boiling benzene; a trace of gelatinous matter at first separated, which was rapidly removed, and, on cooling, the filtrate deposited crystals, which were collected and washed with benzene.

0.1023 gave 10.7 c.c. of nitrogen at 21° and 754 mm.  $N = 11.81$ .

$\text{C}_{15}\text{H}_6\text{O}_5(\text{NO}_2)_4 \cdot \text{C}_6\text{H}_5 \cdot \text{NO}_2$  requires  $N = 12.21$  per cent.

The glistening, orange-coloured needles thus obtained did not melt sharply, for they showed signs of fusion at 150°, and finally melted at 238—240°. Suspecting that this was a nitrobenzene additive compound of the original substance, it was digested with boiling alcohol to remove the nitrobenzene; it dissolved readily, but, on continued heating, crystals separated, which were collected and washed with alcohol.

0.1097 gave 0.1602  $\text{CO}_2$  and 0.0220  $\text{H}_2\text{O}$   $\text{C} = 39.82$ ;  $\text{H} = 2.22$ .  
 0.1227 „ 0.1815  $\text{CO}_2$  „ 0.0225  $\text{H}_2\text{O}$ .  $\text{C} = 40.34$ ;  $\text{H} = 2.03$ .  
 0.1075 „ 11.7 c.c. of nitrogen at  $24^\circ$  and 755 mm.  $\text{N} = 12.12$ .  
 0.1087 „ 11.6 c.c. „  $22^\circ$  „ 760 mm.  $\text{N} = 12.09$ .  
 $\text{C}_{15}\text{H}_6\text{O}_5(\text{NO}_2)_4$  requires  $\text{C} = 40.00$ ;  $\text{H} = 1.35$ ;  $\text{N} = 12.44$  per cent.

It was obtained as a mass of fine, lemon-yellow needles melting at  $239\text{--}241^\circ$ , almost insoluble in boiling alcohol and the usual solvents. Aqueous or alcoholic solutions of the alkalis do not appreciably dissolve it, for it is at once converted into a scarlet salt insoluble in water or alcohol. When digested with boiling acetic anhydride, it yields a colourless, crystalline product, apparently an acetyl derivative, but this could not be examined owing to lack of material. The nitro-compound dyes calico mordanted with alumina, an orange, and, with iron, a brownish-buff shade.

To obtain some insight, if possible, into the nature of this substance, the small quantity remaining was boiled with nitric acid of sp. gr. 1.54; it dissolved but slowly, forming a clear solution, which, when evaporated to a small bulk and diluted with water, deposited *picric acid* in colourless needles melting at  $119\text{--}121^\circ$ .

Attempts to increase the yield of the insoluble nitro-compound by various methods have hitherto been unsuccessful; among these may be cited the employment of nitric acid diluted with acetic acid. Owing to its sparing solubility and its property of dyeing mordanted calico, it seemed possible at first that this was a tetranitrovitexin, but its lack of oxygen cannot be made to agree with this supposition. If its molecular weight be high, the analytical figures, as shown above, approximate to  $\text{C}_{15}\text{H}_6\text{O}_5(\text{NO}_2)_4$ , which would represent a tetranitro-derivative of some oxidation product of the colouring matter. Certainly no such substance is produced during the nitration of parahydroxybenzoic acid, which has been studied for this purpose.

I hope shortly to be in possession of sufficient raw material to undertake a further study of this substance, feeling that this may have an important bearing on the constitution of the colouring matter. With hot nitric acid of sp. gr. 1.54, vitexin gives only picric and dinitrohydroxybenzoic acids.

#### *Action of Alcoholic Potash on the Ethylation Product of Vitexin.*

Attempts to prepare an ethylic ether of vitexin in a pure condition gave unsatisfactory results, the light yellow substance formed being always contaminated with considerable quantities of a resinous decomposition product. Owing to the very ready solubility of both in the ordinary solvents, no method has as yet suggested itself for

their separation. By fractional precipitation of an alcoholic solution with hot water, however, a trace of pale yellow needles was obtained, still slightly impure. The characteristics of this substance reminded one of the ethers of the quercetin and xanthone series, for alcoholic potash yielded a potassium compound, and acetic anhydride a colourless acetyl derivative, the latter extremely soluble. It appears probable that, in vitexin, an hydroxyl group exists which resists ethylation, and is consequently in the ortho-position relatively to a carbonyl group. The methylation of vitexin has also been studied with a like result, but it is hoped that, by varying the conditions of experiment, these difficulties may ultimately be surmounted.

With the hope of obtaining a further clue to the constitution of vitexin, the action of alcoholic potash on the crude product of ethylation was studied. This was effected in the usual manner, boiling for 12 hours, the brown solution being evaporated to dryness, and dissolved in water. After extraction with ether (*E*), the aqueous liquid was saturated with carbonic anhydride, again extracted with ether (*F*), and finally neutralised with acid; the almost colourless precipitate thus obtained was dissolved in ether, the solution evaporated, and the residue crystallised, first from water and then from benzene.

0.1109 gave 0.2647  $\text{CO}_2$  and 0.0632  $\text{H}_2\text{O}$ .  $\text{C} = 65.09$ ;  $\text{H} = 6.33$ .

$\text{C}_6\text{H}_4(\text{OC}_2\text{H}_5)\cdot\text{COOH}$  requires  $\text{C} = 65.06$ ;  $\text{H} = 6.02$  per cent.

This substance crystallised in colourless needles, melted at  $193-195^\circ$ , although sintering slightly below this point, and on fusion with alkali gave parahydroxybenzoic acid. It was evidently parethoxybenzoic acid.

Extract *E*, on evaporation, yielded a small quantity of an oil having the persistent odour of aniseed, and was most probably parethoxybenzaldehyde.

A decoction of the brownish, viscous residue obtained from extract *E* gave the phloroglucinol reaction, although somewhat slowly, and resembled the corresponding products formed by the decomposition of the ethers of morin and luteolin.

### *Dyeing Properties of Vitexin.*

To obtain this sparingly soluble colouring matter in a finely divided condition for these experiments, a known weight was dissolved in alkali, precipitated with acid in the cold, and the paste, after washing, made up to a given bulk with water. Employing woollen cloth mordanted with aluminium, chromium, tin, and iron, the shades given below were obtained; these were of a poor character, due to some extent



to the insoluble nature of the dye. On the other hand, one cannot but be struck with the resemblance in the shades given by vitexin and gentisin, chrysin, and apigenin, colouring matters which do not contain two hydroxyl groups in the ortho-position relatively to one another. This is, therefore, a further corroboration of the results above described.

	Aluminium.	Chromium.	Iron.	Tin.
Vitexin {	Bright yellow, } pale.	Greenish-yellow {	Pale brown, some- what dull.	{ Very pale yellow scarcely dyed.
Gentisin {	Bright yellow, } and pale, scarcely dyed.	Green yellow, dull and pale.		{ Cream colour, scarcely dyed.
Apigenin...	Pure yellow. }	Yellow leaving faint orange tint. }	Chocolate brown.	Undyed.

*More Soluble Constituent of the Wood.*

The dark coloured alcoholic extract *A* obtained in the purification of the crude vitexin (p. 1021), was evaporated to dryness, and the resinous residue powdered and dissolved in boiling absolute alcohol; the greyish, amorphous precipitate which separated on cooling gradually became a tarry mass, and was removed by filtration. The orange-coloured filtrate, when allowed to evaporate spontaneously and absorb moisture from the air, slowly deposited an amorphous, yellow product, which, after being washed with a little absolute alcohol and then with dilute alcohol, was purified by crystallisation from absolute alcohol.

0.1092 gave 0.2400 CO<sub>2</sub> and 0.0518 H<sub>2</sub>O. C = 59.93; H = 5.27.

0.1087 „ 0.2395 CO<sub>2</sub> „ 0.0550 H<sub>2</sub>O. C = 60.08; H = 5.61.

C<sub>16</sub>H<sub>16</sub>O<sub>7</sub> requires C = 60.00; H = 5.00 per cent.

C<sub>18</sub>H<sub>18</sub>O<sub>8</sub> „ C = 59.66; H = 4.97 „

It is a pale primrose-yellow powder, consisting of microscopic needles melting at 245—246°, and is distinguished from vitexin by its ready solubility in boiling alcohol. The alcoholic solution is coloured by ferric chloride in exactly the same way as vitexin, but gives no precipitate with lead acetate, although the basic salt yields a bright canary-yellow deposit. It dissolves in alkali solutions with a very pale yellow colour, and is almost devoid of dyeing property, mordanted calico being but feebly stained by it. With cold sulphuric acid, it gives a pale, yellowish-brown liquid, which, when heated, becomes deep brown at 120°, and at 160—170° acquires an olive-green

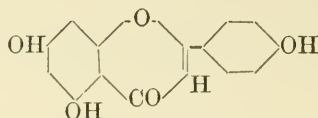
tint. This reaction, almost identical with that of vitexin, points to a close relationship between them. The amount of this product existing in the wood as glucoside must be exceedingly small, for in no case was more than 0.5 gram in a crude condition isolated from a kilogram of the material, and this was considerably reduced on purification. On this account, sufficient was not available for a study of its derivatives, although it was noted that it formed a colourless acetyl compound, which was readily soluble in alcohol and crystallised with some difficulty.

When fused with alkali, it yielded phloroglucinol and parahydroxybenzoic acid, the latter being identified by its melting point, 209—210°, and its reaction with ferric chloride. Examined by Zeisel's method, the substance was found not to contain methoxy-groups, and from the hydriodic acid residue some unchanged colouring matter was recovered. This substance, to which the name *homovitexin* is given will be further examined.

#### *Summary of Results.*

This investigation shows that the wood of *Vitex littoralis* contains two colouring matters in the form of glucosides. Vitexin, which is the most insoluble and also the chief constituent, gives numbers agreeing with the formula  $C_{15}H_{14}O_7$ , or  $C_{17}H_{16}O_8$ , and contains, according to the formula adopted, either five or six hydroxyl groups. With the exception of the acetyl derivative, no other substitution products have as yet been isolated in a pure condition, owing, curiously enough, to their ready solubility and their contamination with decomposition products, which always appear to accompany their formation. On fusion with alkali, vitexin gives phloroglucinol, parahydroxybenzoic and acetic acids, and with potassium hydroxide solution at a lower temperature, phloroglucinol and parahydroxyacetophenone; alcoholic potash behaves similarly. Further, on decomposing, with alcoholic potash, the crude product of its ethylation, parahydroxybenzoic acid, parahydroxybenzaldehyde and a phloroglucinol derivative are obtained. With dilute nitric acid, picric and metadinitroparahydroxybenzoic acids are formed, together with an insoluble nitro-compound, to which the formula  $C_{15}H_6O_5(NO_2)_4$  has been provisionally assigned. The dyeing and other properties of this substance suggest its high molecular weight, and it would appear to be the tetranitro-derivative of an oxidation product of the colouring matter. According to its dyeing properties and the above reactions, it is apparent that vitexin does not contain two hydroxyls in the ortho-position relatively to one another, and in this respect resembles apigenin, chrysin, and gentisin. There is evidence that vitexin con-

tains one hydroxyl in the ortho-position relatively to a carboxyl group, and the formation from it of hydroxyacetophenone suggests the presence of a  $\gamma$ -pyrone ring. Curiously enough, its principal decomposition products are identical with those of apigenin,  $C_{15}H_{10}O_5$ , to which I assigned (Trans., 1897, **71**, 895) the constitution



It would thus appear to be closely related to the latter substance. Although no evidence as yet exists, it is possible that its constitution may be represented by the same formula as apigenin, with a side chain attached. Experiments on the behaviour of apigenin towards nitric acid, a short notice of which has already appeared (*loc. cit.*), will be continued, to throw some light upon this point.\*

The more soluble colouring matter, homovitexin,  $C_{16}H_{16}O_7$ , or  $C_{18}H_{18}O_8$ , which is contained in the wood in very small quantity only, is very closely related to vitexin, which it resembles in numerous reactions and in the similarity of its decomposition products, but differs from it in possessing only feeble dyeing properties. It contains no methoxy-group.

### *The Dyeing Properties of the Wood.*

In studying the dyeing properties of this material, woollen cloth mordanted with aluminium, iron, chromium, and tin was employed. The results are embodied in the table on p. 1031, in which have also been placed for comparison the shades given by old fustic (*Morus tinctoria*) and Weld (*Reseda luteola*), for these among the commercial natural dye-stuffs most nearly approximate in shade to the *Vitex littoralis*.

The most striking property of this dye-stuff is the very yellow tones it produces with chromium and aluminium mordants, these being free from any admixture of red, and possess, if anything, a faint greenish tint. Exposed to light for three months, the chromium and iron mordanted patterns showed no great alteration, whereas the aluminium

\* During some experiments by Prof. Hummel and myself on the dyeing properties of the natural yellow colouring matters, an examination has been made of scoparin which is present in the *Spartium scoparium*. The shades obtained are almost identical with those given by vitexin, and it is interesting to note that the percentage composition of scoparin,  $C_{21}H_{22}O_{10}$  (Stenhouse, *Annalen*, **78**, 15),  $C=58.06$ ,  $H=5.08$ , differs but little from that of vitexin. Although not identical, it is probable that the investigation of scoparin now proceeding will reveal a close relationship between these colouring matters.

	Chromium.	Aluminium.	Tin.	Iron.
<i>Vitex littoralis</i>	{ Dull yellow, slight green tint.	{ Dull yellow, slightly pale.	Pale lemon- yellow.	Dull grey- brown.
Weld.....	{ Full brown- yellow.	{ Bright yellow.	Pale yellow.	{ Deep brown- olive.
Old Fustic ...	„	Yellow olive.	Pale yellow.	{ Deep brown- olive.

and tin shades had very perceptibly faded. The results with mordanted calico were similar, although the colours thus obtained had a slightly brighter character.

Three samples of the wood were examined, with the result that there was some variation in colour strength; the sample last received was the strongest, and this was employed for the above dyeing experiments.

On account of the pure yellow tones it produces, some hope exists that, where these are necessary, this dye-stuff may be of some commercial utility for this purpose. A well-known Leeds firm who have examined a sample, consider that it should have a limited sale at £4 a ton, a value somewhat below that of old fustic, which is at present £4 10s.

During the examination of apigenin and vitexin, it has been shown that these colouring matters are not perceptibly oxidised on passing air through their alkaline solutions, and it seemed of interest to ascertain if this property was in any way connected with their behaviour on exposure to light. Experiments, however, seem to negative this view, for the shades given by aluminium and tin mordants are not fast, and those with chromium and iron possess no great superiority over those obtained from colouring matters which suffer decomposition when oxidised in a similar manner.

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## CII.—*Derivatives of Hesperitin.*

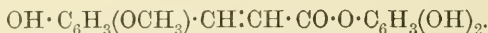
By ARTHUR GEORGE PERKIN, F.R.S.E.

HESPERITIN occurs in the form of its glucoside hesperidin, in many varieties of the *Aurantiacæ*, being contained in the citron and unripe orange, the bitter variety being very suitable for its preparation.

It has been examined by E. Hoffmann (*Ber.*, 1876, 9, 685), who dis-

covered the glucoside nature of hesperidin, and showed that hesperitin itself is decomposed by potassium hydroxide solution at  $100^{\circ}$  into phloroglucinol and hesperitinic acid,  $C_{10}H_{10}O_4$ ; these results pointed to the constitution  $C_6H_5O_2 \cdot O \cdot C_{10}H_9O_3$ .

Tiemann and Will (*Ber.*, 1881, 14, 948) confirmed the work of Hoffmann, and also proved that hesperitinic acid is identical with isoferulic acid, the monomethyl ether of dihydroxycinnamic acid. Hesperitin was, therefore, the monomethyl ether of dihydroxycinnamyl-phloroglucinol.



Hesperitin crystallises in almost colourless needles melting at  $226^{\circ}$  and having an intensely sweet taste; its alkaline solutions, also, are nearly colourless, having at most a very faint yellow tint, and it does not dye mordanted calico.

At first, experiments were undertaken to determine the behaviour of hesperitin with alcoholic solutions of the alkali acetates, for in this way it has been shown (*Proc.*, 1898) that quercetin and analogous substances yield peculiar salts. Its apparently somewhat close relationship to phloretin, however, suggested further work, with the hope of explaining the somewhat peculiar properties of disazobenzenephloretin (*Trans.*, 1897, 71, 1151).

#### *Disazobenzenehesperitin.*

To a solution of hesperitin in dilute sodium carbonate, a slight excess of diazobenzene sulphate solution was added, and the deep red precipitate collected, washed, and dried. Owing to the exceedingly resinous nature of this product, all attempts to obtain it in a pure state by the usual methods failed, and it seemed as if experiments in this direction must be abandoned; finally, however, the acetylation of the crude product suggested itself, the acetyl derivatives of such compounds being, as a rule, more easy to purify. It was therefore dissolved in a very small quantity of hot acetic anhydride, and boiled with it for 6 hours; when cold, it was diluted with alcohol, and the crystalline powder deposited on standing overnight was collected, washed with alcohol, and crystallised from acetic acid. As the glistening needles thus obtained showed signs of melting at  $200^{\circ}$ , but did not completely melt until  $236-238^{\circ}$ , it seemed probable that the substance had been incompletely acetylated. It was, therefore, again digested with a little boiling acetic anhydride, when the solution became semi-solid on continued heating, owing to the separation of fine, hair-like needles. On adding alcohol, and, after some hours, collecting the crystals, and washing them with alcohol, they melted



sharply at 240—242°, and showed no sign of decomposition at a lower temperature. Unfortunately, the yield was poor, being equal to but 10 per cent. of the hesperitin employed.

0·1142 gave 10·6 c.c. nitrogen at 22° and 760 mm.  $N = 10·51$ .

$C_2H_3O \cdot C_{16}H_{11}O_6(C_6H_5N_2)_2$  requires  $N = 10·15$  per cent.

*Acetyl disazobenzenehesperitin* forms an ochre-coloured mass of glistening needles sparingly soluble in boiling acetic acid, almost insoluble in alcohol. Dilute alkali solutions do not dissolve it in the cold, but on heating it is decomposed with formation of an orange-red liquid.

To determine with certainty the number of acetyl groups present in this substance, it was boiled for a short time with dilute alcoholic potash and the solution neutralised with acid. After dilution with hot water and cooling, the precipitate of the free disazo-compound was collected and weighed.

0·5032 gave 0·4670. Found 92·80.

$C_2H_3O \cdot C_{16}H_{11}O_6(C_6H_5N_2)_2$  requires  $C_{16}H_{12}O_6(C_6H_5N_2)_2 = 92·39$  per cent.

It is, therefore, a *monacetyl* derivative.

The disazobenzenehesperitin formed was analysed.

0·1115 gave 10·9 c.c. nitrogen at 21° and 762 mm.  $N = 11·15$ .

$C_{16}H_{12}O_6(C_6H_5N_2)_2$  requires  $N = 10·98$  per cent.

*Disazobenzenehesperitin* is fairly soluble in boiling nitrobenzene, separating from the concentrated solution in beautiful, glistening, red needles; these are deposited in larger quantity if the nitrobenzene solution is diluted with alcohol, as it is almost insoluble in the latter. When heated, it sinters at 240°, and melts with decomposition at 246—247°. Alkali solutions dissolve it with an orange-red, and sulphuric acid with a scarlet, coloration. As the acetyl derivative of this substance was previously obtained from the crude product of the reaction of hesperitin with diazobenzene, a small quantity was now prepared by the action of boiling acetic anhydride on the pure substance with the object of being certain that a fully acetylated derivative had been prepared in the previous experiment. It was somewhat slowly attacked, and at the conclusion of the action crystals separated at the boiling temperature. These were collected and washed with alcohol.

0·1355 gave 12·3 c.c. nitrogen at 24° and 759 mm.  $N = 10·17$ .

The monacetyl compound requires  $N = 10·15$  per cent.

It melted at 240—242°, was identical with the acetyl derivative above described, and is consequently the final product of the action of acetic anhydride on disazobenzenehesperitin.

The results indicate that hesperitin contains three hydroxyl groups, two of them in the disazobenzene derivative being neutralised in consequence of their ortho-position relatively to the diazobenzene groups.

*Acetylhesperitin.*

Ciamician and Silber (*Ber.*, 1898, 28, 1393) have shown that phloretin yields a tetracetyl derivative, whereas the diazobenzene derivative, like that of hesperitin, indicates but three such, and it was thus interesting to prepare, if possible, an acetyl compound of the latter.

Hesperitin was gradually added to boiling acetic anhydride (the use of sodium acetate is not beneficial), and when it had dissolved, the clear solution was boiled for 6 hours longer; a portion of the acetic anhydride was now removed by evaporation, and the residual liquid cooled somewhat and diluted with alcohol. Crystals were slowly deposited, the separation being facilitated by agitation from time to time; after a week, the crystals were collected and washed with alcohol, and purified by crystallisation from a mixture of acetic acid and alcohol until the melting point was constant.

0.1148 gave 0.2593 CO<sub>2</sub> and 0.0490 H<sub>2</sub>O. C = 61.59; H = 4.74.

0.1116 „ 0.2530 CO<sub>2</sub> „ 0.0495 H<sub>2</sub>O. C = 61.82; H = 4.92.

C<sub>16</sub>H<sub>11</sub>O<sub>6</sub>(C<sub>2</sub>H<sub>3</sub>O)<sub>3</sub> requires C = 61.68; H = 4.67 per cent.

C<sub>16</sub>H<sub>10</sub>O<sub>6</sub>(C<sub>2</sub>H<sub>3</sub>O)<sub>4</sub> „ C = 61.28; H = 4.68 „

Acetylhesperitin forms colourless, silky needles melting at 127—129°, readily soluble in acetic acid, somewhat sparingly in alcohol; by slow crystallisation, it can be obtained as prismatic needles of large size.

The above analyses agree more nearly with those required for a triacetyl than a tetracetyl derivative, but the difference was not decided enough for this to be considered certain. The determination of the acetyl groups presented some difficulty, as hesperitin is so readily decomposed by the ordinary reagents at anything like the boiling heat. A rapid determination, made by decomposing the acetyl compound with sulphuric acid in boiling acetic acid, gave the following result.

1.0822 gave 0.7635 gram. Found 70.55.

The theory for 3 acetyls requires C<sub>16</sub>H<sub>14</sub>O<sub>6</sub> = 70.56 per cent.,

but the product was so discoloured that the accuracy of the determination was doubted. A determination in the cold, however, gave results which may be considered as correct. 1.006 grams of acetylhesperitin, dissolved in 12 c.c. of acetic acid, was treated in the cold with 1 c.c. of sulphuric acid, the mixture being kept in a stoppered vessel for

48 hours ; the solution, after exposure to moist air for 48 hours, had deposited crystals, and more separated on adding water very cautiously ; these were collected, and weighed 0·7065 gram or 70·22 per cent. That the product, although of a slight red tint, was hesperitin was evident from its melting point, 218—220° (hesperitin melts at 226°). In a second experiment, 1·3 grams of the acetyl compound gave 0·9180 gram of hesperitin, or 70·61 per cent. These results, therefore, corroborate those given by the diazobenzene derivative, and show that hesperitin,  $C_{16}H_{14}O_6$ , contains three hydroxyl groups.

An experiment was made to determine if hesperitin, like maclurin and phloretin, can be converted into a coumarin compound by the prolonged action of acetic anhydride and sodium acetate (Ciamician and Silber, *Ber.*, 1894, 28, 1393). In this manner, a very soluble, colourless product was formed, which has at present refused to crystallise, whereas in the case of maclurin and phloretin sparingly soluble substances are formed. A very small quantity of hesperitin was available for this purpose, and it is possible that a variation in the conditions might produce a compound of this nature ; on the other hand, the results given in this paper indicate such a change to be unlikely.

*Compounds of Hesperitin with Potassium and Sodium Acetates.*

It has been pointed out in a previous communication (*loc. cit.*) that certain colouring matters, when treated with the alkali acetates in presence of alcohol, yield mono-substituted salts ; experiment showed that hesperitin behaved in a somewhat similar manner. When a concentrated alcoholic solution of hesperitin is treated with potassium acetate, crystals of a salt separate rapidly, and, being insoluble, may be collected and washed with alcohol. The yield was 1·78 grams salt from 2 grams of hesperidin. Analyses were made of separate preparations, which were dried at 160°.

0·8164 gave 0·1026  $K_2SO_4$ .  $K = 5·63$ .

0·7770 „ 0·1000  $K_2SO_4$ .  $K = 5·77$ .

At first sight, this salt appeared to have the formula  $C_{32}H_{27}O_{12}K$ , or a double molecule of hesperitin with one hydrogen displaced by the metal ( $K = 6·07$ ). As, however, further analyses again gave this somewhat low percentage, the yield of hesperitin obtained on decomposing the salt with acid was determined.

0·9100 gave 0·7740 hesperitin. Found 85·05.

2·8650 „ 2·4270 „ „ 84·71.

0·9966 „ 0·8510 „ „ 85·38.

$C_{32}H_{27}O_{12}K$  requires  $C_{16}H_{14}O_6 = 94·08$  per cent.

$(C_{16}H_{14}O_6)_2, C_2H_3O_2K$  requires  $C_{16}H_{14}O_6 = 86·03$  per cent.

It appears, therefore, that this salt is a compound of 2 molecules of hesperitin with 1 of potassium acetate. That no decomposition had ensued during the formation of this substance was evident, for the mother liquors from its preparation contained only a trace of unaltered hesperitin, and that regenerated from the salt by acid had the normal melting point.

The salt forms colourless needles almost insoluble in alcohol and cold water, but decomposed by boiling water with formation of hesperitin. This was identified by its melting point, 223—225°, and the following analysis.

0.1161 gave 0.2707  $\text{CO}_2$  and 0.0490  $\text{H}_2\text{O}$ .  $\text{C} = 63.58$ ;  $\text{H} = 4.69$ .

$\text{C}_{16}\text{H}_{14}\text{O}_6$  requires  $\text{C} = 63.57$ ;  $\text{H} = 4.63$  per cent.

An estimation of the hesperitin set free in this manner showed that the reaction was somewhat complex, for 1.3382 gram of salt gave but 0.6930 gram of hesperitin, or 51.8 per cent.; the pale yellow filtrate was now treated with acid, when a precipitate of 0.4300 gram of hesperitin, melting at 223—226°, was obtained, giving a total yield of 83.93 per cent. It thus appears probable that boiling water decomposes this salt with elimination at first of potassium acetate, and that this then reacts with a portion of the hesperitin, forming a potassium salt soluble in water, acetic acid being liberated at the same time. The sodium compound formed from hesperitin and sodium acetate crystallised in colourless needles closely resembling the potassium salt.

0.6435 gave 0.0730  $\text{Na}_2\text{SO}_4$ .  $\text{Na} = 3.67$ .

$(\text{C}_{16}\text{H}_{14}\text{O}_6)_2, \text{NaC}_2\text{H}_3\text{O}_2$  requires  $\text{Na} = 3.35$  per cent.\*

Maclurin and phloretin, however, yield no insoluble compounds in this manner.

#### *Potassium and Sodium Hesperitin.*

The formulæ of the substances just described suggested that the molecular weight of hesperitin was twice that usually assigned to it, or  $\text{C}_{32}\text{H}_{28}\text{O}_{12}$ , and as it was found that potassium and sodium deriva-

\* Further experiments on the salts of quercetin and morin obtained by means of the alkali acetates (*loc. cit.*) show that they are true salts and not constituted like the hesperitin compounds. Thus potassium quercetin has the formula  $\text{C}_{15}\text{H}_9\text{O}_7\text{K}$ , as on decomposition with acids it gives 88.54 per cent. of quercetin (theory = 88.3). The power of forming salts in this manner is not confined to the quercetin group, but is also possessed by some other colouring matters. In this reaction, for instance, alizarin gives  $\text{C}_{14}\text{H}_7\text{O}_4\text{K}$  (found  $\text{K} = 14.01$ , theory  $\text{K} = 14.02$ ), a crystalline, violet-coloured salt, and from anthragallol the compound  $\text{C}_{14}\text{H}_7\text{O}_5\text{K}$  (found  $\text{K} = 13.26$ , theory  $\text{K} = 13.26$ ) is obtained in small, blue-black needles. Hæmatein and brazilein possess a similar property, and experiments are in progress with regard to other mordant dye-stuffs.

tives could be prepared, these were studied with the object of elucidating this point.

When hesperitin was added to a solution of potassium hydrogen carbonate and the mixture boiled, it gradually dissolved, forming a pale yellow liquid, which, on further heating, deposited a colourless, crystalline powder; the addition of a fresh quantity of the solid bicarbonate to the hot solution was frequently of advantage. When cold, the product was collected, washed with water, and dried at 160°.

0.5617 gave 0.0760  $K_2SO_4$ .  $K = 6.06$ .

$C_{32}H_{27}O_{12}K$  requires  $K = 6.07$  per cent.

*Potassium hesperitin* forms minute, colourless plates insoluble in cold water and readily decomposed by dilute acids, yielding hesperitin.

*Sodium hesperitin*, prepared in a similar manner, closely resembles the above salt.

0.8225 gave 0.0940  $Na_2SO_4$ .  $Na = 3.70$ .

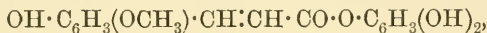
0.6730 „ 0.0820  $Na_2SO_4$ .  $Na = 3.94$ .

$C_{32}H_{27}O_{12}Na$  requires  $Na = 3.67$  per cent.

These results indicate that the molecular weight of hesperitin is represented by the formula  $C_{32}H_{23}O_{12}$ ; consequently, the formulæ of its derivatives must also be doubled. The acetyl, tetrazobenzene, and acetyltetrazobenzene compounds will accordingly be respectively  $[C_{16}H_{11}O_6(C_2H_3O)_3]_2$ ,  $[C_{16}H_{12}O_6(C_6H_5N_2)_2]_2$ , and



If hesperitin had the simple formula  $C_{16}H_{14}O_6$ , it would be evident that Tiemann and Will's constitution (*loc. cit.*),



was correct, and this would be further supported by the experiments of Hoffmann, who obtained from it an almost quantitative yield of phloroglucinol and hesperitinic acid (*loc. cit.*). The expression of this by a double formula is difficult, for were hesperitin but a polymerised substance of this constitution, it might be expected to yield di- and not mono-potassium and sodium salts; whether these result merely from the neutralisation of a carboxyl group or are in any way related to the mono-substituted salts of quercetin and other colouring matters (*loc. cit.*) is not certain, but the study of the latter compounds, now in hand, will tend to elucidate this point.

Owing to the costly nature of hesperitin and the difficulty of obtaining just now suitable raw material for its preparation, it will not be further studied at present.

It is interesting to note that the azobenzene derivative of hesperitin on acetylation, gives a true indication of the hydroxyl groups which hesperitin itself contains, and this, in previous communications, has also



been shown to be the case with the azobenzene compounds of maclurin, cotoin, apigenin, chrysin, euxanthone, and gentisin. The fact, already alluded to in this paper, that phloretin in this manner gives an abnormal result, points to the probability that its constitution differs in some respects from that assigned to it at present.

CLOTHWORKERS' RESEARCH LABORATORY,  
DYEING DEPARTMENT,  
YORKSHIRE COLLEGE.

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# ANNUAL GENERAL MEETING,

MARCH 31, 1898.

Professor DEWAR, President, in the Chair.

Mr. W. G. McMILLAN and Dr. THORNE were appointed Scrutators, and a ballot was opened for the election of Officers and Council for the ensuing year, the ballot being closed at the conclusion of the President's address.

The PRESIDENT, in beginning his address, remarked that the papers submitted to the Society during the past session included original works in all branches of Chemical Science. They have been contributed, not only from the laboratories of the older Universities of Oxford and Cambridge, but also from the University Colleges and other institutions throughout the country. The publications of the Society are, therefore, a complete record of English Chemical Science, and of the researches pursued at different educational centres throughout the country.

The Proceedings is now the medium of publication, not only of abstracts of papers which will subsequently appear in the Transactions, but also of the rapid publication of short papers and preliminary notices.

The rule, which came into force last year, requiring that authors shall deposit their papers and abstracts with the Secretaries before they are officially announced for reading at a meeting, has worked well; it has made it possible to expedite the publication of the Proceedings, and to send advance proofs to the authors for correction.

The meetings have been well attended, the meeting-room being often quite full. Occasionally, interesting discussions have taken place, but as so many of our papers deal with details and matters of fact, anything like a debate must necessarily be of rare occurrence.

The following past Presidents, Lord Playfair, Dr. A. W. Williamson, Sir E. Frankland, Dr. W. Odling, Sir F. A. Abel, Dr. J. H. Gladstone, Sir J. H. Gilbert, this year complete a connection of 50 years

with the Society. To mark its sense of the great services they have rendered to Chemical Science, the Council has resolved to entertain them, in the name of the Society, at a dinner on June 9th, given to commemorate their half-century of Fellowship of the Society.

During the past year the Council has had under consideration the question of a revision of the Bye-laws. A Committee was appointed early in the year, which has met several times during the session, but, in view of the wider questions which have occupied the attention of the Council, they have not been able to complete their report.

During the session a section of the Fellows residing at a distance from London have expressed a desire to take part in the election of Officers and Council, without being forced to undertake a journey to London to register their votes at the Annual General Meeting. A Memorial was drawn up, asking the Council to prepare and lay before the Society a Bye-law enabling Fellows to record their votes by post. This Memorial was signed by 540 Fellows, of whom 400 resided outside the London district. In the meantime, the Bye-law Committee had taken steps to ascertain the powers of the Society in this matter under their Charter. They were legally advised that any Bye-law framed to admit voting by post or proxy would be repugnant to the Charter, and therefore invalid.

When the Memorial was presented to the Council, a covering letter contained another suggestion, viz., that it might probably be necessary to obtain a Supplemental Charter, in order to enable the Council to carry out the wishes of the Memorialists. This suggestion was seriously considered by the Council, and further legal opinion was taken on the subject. They were advised that no application for a Supplemental Charter which was not supported by the practically unanimous wish of the Fellows would be listened to by the Privy Council. They have since been further advised that it would be *ultra vires* on their part to expend any part of the funds of the Society in applying for a Supplemental Charter. All the documents relating to the Memorial and the various legal opinions, together with the decisions of the Council, have already appeared in the Proceedings, pp. 1, 33, 61.

The following eminent foreign chemists, whose names are familiar to us all as of those who have advanced knowledge in various departments of our science, were elected Foreign Members in January of this year, bringing the total number of Foreign Members of the Society up to 38: Professors S. Arrhenius; Th. Curtius; A. P. N. Franchimont; W. Körner; W. Markownikoff; N. A. Menshutkin; H. Moissan; W. Ostwald; F. M. Raoult; I. Remsen; W. Spring; L. J. Troost; P. Waage; J. D. van der Waals. The Society has lost a Foreign Member by death: Professor Victor Meyer, one of the most brilliant and original of the modern school of chemists. The Kekulé

Memorial Lecture has been delivered by Professor Japp. It has been resolved that the Memorial Lectures delivered up to 1896 shall be bound and published as Vol. I. of the Society's Memorial Lectures as soon as possible.

The Council have nominated the Treasurer and Editor as delegates for the Society to the National Committee appointed by the Royal Society to prepare a Catalogue of Scientific Literature.

The remainder of the President's address was devoted to an account of recent advances in Low Temperature Research, which will subsequently appear in the Transactions.

The numerical strength of the Society was as follows :—

Number of Fellows, March 31st, 1897 .....	2079
„ „ since elected .....	114
„ „ reinstated by Council.....	4
	<hr/>
	2197
Removed on account of non-payment of two annual subscriptions .....	16
Withdrawn .....	22
Deaths .....	19
	<hr/>
	57
Number of Fellows, March 31st, 1898 .....	2140
Foreign Members .....	38

Fourteen Foreign Members were elected during the year.

The names of those removed were :—J. Burgess ; T. R. Carswell ; L. B. Dutson ; W. T. Gibbs ; R. B. Greaves ; T. B. Hall ; E. H. Hill ; P. Hudson ; C. W. Lee ; W. M. Martin ; R. A. Rouillard ; J. W. Slater ; J. W. Smith ; R. M. Sumner ; W. Virtue ; W. H. Walden.

The following have withdrawn :—C. L. Barnes ; J. C. Cain ; W. Johnstoun Coombes ; E. C. Copas ; J. H. Freeman ; D. St. J. Grant ; A. L. Guiterman ; James Hall ; John Howard ; R. E. Hughes ; J. W. James ; A. Luty ; A. Kinninmont ; D. J. Morgan ; E. W. Napper ; E. W. Prevost ; Frederick Quincke ; D. H. Richards ; A. E. Richardson ; R. Routledge ; W. E. Sim ; E. E. H. Thorne ; C. A. Warren.

The following have died :—J. J. Bowrey ; G. W. Child ; E. H. Gaskell ; B. H. Gibbins ; W. A. L. Hammersley ; S. J. Harris ; W. L. Hiepe ; Walter Jardine ; G. A. Keyworth ; M. H. Lackersteen ; Samuel Lees ; Herman Lescher ; Thomas Mitchell ; Howard Newton ; F. M. Rimmington ; J. W. Rodger ; Tarapasanna Roy ; W. J. Saint ; James Napier.

The number of communications made to the Society during the year was 127.

One hundred and fourteen papers were published in the Transactions for 1897, occupying 1204 pages, whereas in the preceding year 117 papers were published, occupying 1702 pages.

The following were the statistics relating to the Abstracts.

PART I.		
	Pages.	No. of Abstracts.
Organic Chemistry .....	648	1049
PART II.		
General and Physical Chemistry .....		324
Inorganic Chemistry .....		270
Mineralogical Chemistry .....		192
Physiological Chemistry.....		168
Chemistry of Vegetable Physiology and Agri- culture .....		158
Analytical Chemistry.....		414
Total in Parts I. and II. ....	612	1526
	<hr/> 1260	<hr/> 2575

Eight hundred and fifty volumes had been borrowed from the Library. The additions comprised 78 books, 282 volumes of periodicals, and 36 pamphlets.

The President then gave a short account of some low temperature phenomena, which he hoped to discuss more fully in his valedictory address to the Fellows next year.

Sir W. CROOKES, F.R.S., proposed a vote of thanks to the President, coupled with the request that he would allow his address to be printed in the Transactions.

Dr. W. J. RUSSELL, F.R.S., seconded the motion, which was carried by acclamation.

The PRESIDENT having returned thanks,

Dr. THORPE, F.R.S., the treasurer, gave an account of the balance sheet, which he laid before the Society, duly audited.

The receipts had been:—By admission fees and subscriptions, £3827; by sale of Journal and advertisements, £686 3s. 6d.; and by dividends on invested capital, £414 6s. 0d. The expenses had been:—On account of the Journal, £2963 11s. 1d.; on account of the Proceedings, £278 7s. 10d.; on account of the General Index, £182 18s. 1d.; on account of the Library, £307 4s. 9d.; House expenses, £203 6s. 7d.; the total expenditure being £4807 6s. 8d. Grants amounting to £150 had been made to Fellows from the Research Fund during the year. (For Balance Sheet see pp. 1044—1046.



Dr. GLADSTONE, F.R.S., proposed that the thanks of the Fellows be tendered to the Treasurer for his services during the past year; this motion was seconded by Dr. STEVENSON, and carried.

The TREASURER, in responding, proposed a vote of thanks to the auditors.

Dr. ATKINSON seconded the motion, which was unanimously adopted, and acknowledged by Mr. R. J. FRISWELL.

Mr. D. HOWARD proposed a vote of thanks to the Officers and Council.

Mr. CASSAL seconded the motion, which was unanimously adopted.

Prof. THOMSON, F.R.S., responded on behalf of the Council.

Dr. B. DYER proposed a vote of thanks to the Editor, Sub-Editor, Abstractors, and Indexers, which was seconded by Mr. R. J. FRISWELL, and carried.

Mr. GROVES, F.R.S., responded.

The Scrutators having presented their report to the President, he declared that the following had been duly elected:—

*President*: James Dewar, M.A., LL.D., F.R.S.

*Vice-Presidents who have filled the office of President*: Sir F. A. Abel, Bart., K.C.B., D.C.L., F.R.S.; H. E. Armstrong, Ph.D., LL.D., F.R.S.; A. Crum Brown, D.Sc., LL.D., F.R.S.; Sir W. Crookes, F.R.S.; Sir E. Frankland, K.C.B., D.C.L., F.R.S.; Sir J. H. Gilbert, Ph.D., LL.D., F.R.S.; J. H. Gladstone, Ph.D., D.Sc., F.R.S.; A. Vernon Harcourt, M.A., D.C.L., F.R.S.; H. Müller, Ph.D., LL.D., F.R.S.; W. Odling, M.B., F.R.S.; W. H. Perkin, LL.D., Ph.D., F.R.S.; Lord Playfair, G.C.B., LL.D., F.R.S.; Sir H. E. Roscoe, LL.D., F.R.S.; W. J. Russell, Ph.D., F.R.S.; A. W. Williamson, LL.D., F.R.S.

*Vice-Presidents*: F. R. Japp, M.A., LL.D., F.R.S.; G. D. Liveing, M.A., D.Sc., F.R.S.; William Ramsay, Ph.D., LL.D., F.R.S.; J. Emerson Reynolds, M.D., D.Sc., F.R.S.; John M. Thomson, F.R.S.; William A. Tilden, D.Sc. F.R.S.;

*Secretaries*: Wyndham R. Dunstan, M.A., F.R.S.; W. P. Wynne, D.Sc., F.R.S.

*Foreign Secretary*: Raphael Meldola, F.R.S.

*Treasurer*: T. E. Thorpe, LL.D., F.R.S.

*Other Members of Council*: P. Phillips Bedson, D.Sc.; E. J. Bevan; H. J. H. Fenton, M.A.; W. Gowland; Otto Hehner; C. T. Heycock, M.A., F.R.S.; D. Howard; Herbert McLeod, F.R.S.; Rudolph Messel, Ph.D.; H. Forster Morley, M.A., D.Sc.; Alexander Scott, M.A., D.Sc.; Arthur Smithells, B.Sc.

## THE TREASURER IN ACCOUNT WITH THE CHEMICAL

Dr.

	£	s.	d.	£	s.	d.
Balance at Bank, March 27th, 1897 .....	911	14	3			
„ in hands of Treasurer .....	0	4	0			
				911	18	3
Receipts by Life Compositions, Admission Fees and Subscriptions from March 27th, 1897, to March 25th, 1898:—						
Life Compositions—8 at £30; 1 at £15; 3 at £12; 6 at £10.....	201	0	0			
113 Admission Fees .....	452	0	0			
16 Subscriptions for 1896 at £2 .....	32	0	0			
487 „ „ 1897 „ £2.....	974	0	0			
3 „ „ „ £1.....	3	0	0			
1,076 „ „ 1898 „ £2.....	2,152	0	0			
13 „ „ „ £1.....	13	0	0	3,827	0	0
Sale of Journals .....	640	10	6			
„ Proceedings .....	12	19	6			
Proceeds of Advertisements in Journal .....	34	13	6			
				688	3	6
Subscription from the Society of Chemical Industry to June, 1897 .....	10	10	0			
„ „ „ Public Analysts to January 1st, 1898 .....	12	12	0			
„ „ „ Physical Society to January 1st, 1898 .....	20	9	6			
„ „ „ Institution of Electrical Engineers .....	1	11	6			
				45	3	0
Repayment of Income Tax.....				14	1	10
Year's Dividends on £6,730 Metropolitan Board of Works 3½ per cent. Stock .....	227	14	0			
„ „ £4,000 Consols.....	106	6	8			
„ „ £1,050 London and North-Western Railway Debenture Stock .....	30	9	0			
„ „ £1,520 14s. 3d. Cardiff Corporation Stock .....	44	2	1			
Interest on £1,000 Bank Deposit .....	5	14	3			
				414	6	0

*Assets*

March 25th, 1898.

Balance at Bank (Current Account) .....	1,093	5	11
„ „ (on Deposit) .....	1,300	0	0
„ in hands of Treasurer .....	0	4	0
Metropolitan Board of Works 3½ per cent. Stock .....	6,730	0	0
2½ per cent. Consols.....	4,000	0	0
London and North-Western Railway Converted Stock .....	1,050	0	0
Cardiff Corporation 3 per cent. Stock.....	1,520	14	3
	<u>£15,694</u>	<u>4</u>	<u>2</u>

£5,900 12 7

SOCIETY, FROM MARCH 27TH, 1897 TO MARCH 25TH, 1898.

CR.

*Expenses on Account of the Journal.*

	£	s.	d.	£	s.	d.
Salary of Editor .....	250	0	0			
" Sub-Editor .....	290	0	0			
" Sub-Editor's Assistant .....	10	10	0			
Editorial Postages .....	8	5	5			
Abstractors' Fees .....	295	5	3			
Periodicals for Abstractors .....	11	7	0			
Printing of Journal .....	(Harrison, £283 12s. 6d. ; Clay & Sons, £1,324 3s. 8d.)	1,607	16	2		
Distribution of Journal by Printers .....	327	7	6			
Society .....	9	13	6			
Authors' Copies .....	(Harrison, £10 9s. 6d. ; Clay & Sons, £88 9s. 6d.)	98	19	0		
Indexers' Fees (1897 Index) .....	59	11	8			
Photogravure Portraits.....	(Pasteur, £24 8s. 0d. ; Kekulé, £26 14s. 9d.)	51	2	9		
Memorial Lectures.....	29	14	9			
Additional Portraits of Kopp .....	3	18	1			
				2,963	11	1
Printing of Proceedings.....	(Harrison, £32 9s. 9d. ; Clay & Sons, £151 12s. 4d.)	184	2	1		
Distribution of Proceedings and List of Fellows .....	89	15	9			
Shorthand Reports .....	4	10	0			
				278	7	10
Publishers' Commission.....				65	6	11
Advertising Agents' Commission .....				5	4	0

*Expenses on Account of the General Index.*

Salaries .....	179	18	0			
Petty expenses .....	3	0	1			
				182	18	1

*Expenses on Account of the Library.*

Salary of Library Attendant .....	42	2	6			
Books and Periodicals .....	183	16	3			
Binding .....	81	6	0			
				307	4	9
Salary of Assistant Secretary.....				174	3	4
Pension to Mr. Hall .....				130	0	0
Miscellaneous Printing.....	(Clay & Sons, £84 6s. 5d. ; Harrison, £2 2s. 9d.)	86	9	2		
Printing List of Fellows (Harrison) .....		30	15	0		
Stationery .....		1	16	1		
Expenses on Account of Dinner on March 31st, 1897 .....		17	10	0		
Legal Charges .....		1	11	6		
Portrait of Dr. Armstrong... ..		4	4	0		
Supply of Electric Current for Lecture .....		2	12	6		

*House Expenses.*

Providing Refreshments.....	19	17	11			
Lighting the Building.....	(Gas, £20 18s. 4d. ; Electric Light, £24 16s. 6d.)	45	14	10		
Heating the Building (Coals) .....	12	1	2			
Cleaning .....	10	0	0			
Repairs .....	6	5	9			
New Electric Light Lamps .....	2	13	9			
Typewriter .....	21	7	0			
Petty House Expenses .....	14	0	5			
House Porter's Wages .....	65	0	0			
" Uniform .....	3	17	6			
Annual Fee to Gate Porter .....	2	2	0			
Inhabited House Duty .....	0	6	3			
				203	6	7
Bank Charges on Country and Foreign Drafts .....				0	17	3
Treasurer's Stamps and Drafts .....				9	11	2
" Assistant.....				10	0	0
Postage Account: Office Postages, £6 5s. 10d. ; Postal Cards and Stamped Envelopes (Clay), £24 7s. 7d. ....				30	13	5
Secretarial Postages .....				1	0	0
Transferred to Deposit Account .....				300	0	0
Balance at Bank (Current Account) .....				1,093	5	11
" in hands of Treasurer .....				4,807	6	8
				£5,900	12	7

Audited with vouchers and found correct. } F. D. CHATTAWAY.  
25th March, 1898. } HORACE T. BROWN.  
R. J. FRISWELL.

## THE TREASURER OF THE CHEMICAL SOCIETY IN ACCOUNT WITH THE RESEARCH FUND.

Dr.

FROM MARCH 27TH, 1897, TO MARCH 25TH, 1898.

Cr.

		£ s. d.		£ s. d.		£ s. d.	
1897.							
Mar. 27.	Balance at Bank, March 27, 1897			61	3	1	
	Year's Dividends on £4,400 Metropolitan Board of Works 3½ per cent. Stock.....	148	17	4			
	Year's Dividends on £1,000 North British Railway 4 per cent. Stock.....	38	13	4			
	Year's Dividends on £1,034 Great Western Railway 2½ per cent. Stock.....	24	19	10			
	Repayment of Grant.....			212	10	6	
	Repayment of Income Tax .....			25	0	0	
	<i>Assets.</i>			6	9	4	
1898.							
Mar. 25.	Balance at Bank.....	135	2	11			
	Metropolitan Board of Works 3½ per cent. Stock.....	4,400	0	0			
	North British Railway 4 per cent. Stock.....	1,000	0	0			
	Great Western Railway Debenture Stock .....	1,034	0	0			
		<u>£6,569</u>	<u>2</u>	<u>11</u>			
							<u>£305 2 11</u>
1897.							
Mar. 31.	Honorarium with Longstaff Medal to Prof. W. Ramsay .....						
June 21.	Grants to H. B. Baker .....			25	0	0	
	Dr. F. D. Chattaway .....			10	0	0	
	Prof. A. E. Dixon .....			10	0	0	
	Dr. J. J. Dobbie .....			20	0	0	
	Dr. J. J. Sudborough .....			10	0	0	
	Dr. G. Young .....			10	0	0	
Dec. 21.	H. A. Auden .....			10	0	0	
	F. C. Garrett .....			10	0	0	
	W. J. Sell .....			15	0	0	
	Dr. J. J. Sudborough .....			20	0	0	
	Dr. James Walker .....			10	0	0	
							<u>65 0 0</u>
1898							
Mar. 25.	Balance at Bank .....						135 2 11
							<u>£305 2 11</u>
							<u>£305 2 11</u>

Audited with vouchers  
and found correct.  
25th March, 1898.

F. D. CHATTAWAY.  
HORACE T. BROWN.  
R. J. FRISWELL.

## OBITUARY NOTICES.

W. L. HIEPE, who was born in March, 1855, at Wiesbaden, studied chemistry there under Fresenius, and subsequently at the University of Berne; whilst at Berne, he became assistant to Professor Forster at the Astronomical Observatory, and subsequently took his degree of Phil. Doc. at the University. In 1877, he came to England as assistant to Dr. A. Hill, the Medical Officer of Health, Birmingham, which position he filled until about 1885, when he became assistant to Mr. Frank Faulkner; in the latter capacity, he became a specialist in the science and practice of brewing. In 1888, he set up in practice for himself in Manchester, and in 1895 he and Dr. A. K. Miller united their separate practices. Dr. Hiepe read several papers before the North of England, and the Midland Institutes of Brewing, and in 1896 filled the position of President to the former Society.

Dr. Hiepe died suddenly at his residence at Withington, Manchester, on February 13th of this year.

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JAMES WYLLIE RODGER.—By the death of James Wyllie Rodger, at the early age of twenty-nine, Chemical Science, and especially that section of it which is more immediately related to physics, has lost one of the most promising and most enthusiastic of its cultivators.

Mr. Rodger was born at Stewarton, in Ayrshire, on December 11th, 1867. After passing through the public school of his native place, he was sent to the well-known Academy at Kilmarnock, where, under the stimulating influence of Dr. Dickie, his taste and aptitude for experimental science were quickly made manifest. In 1884, he gained a free studentship at the Royal College of Science, or, as it was then called, the Normal School of Science, South Kensington. As a student at the College his career was exceptionally brilliant, and such class distinctions as were open to him he gained in rapid succession. In 1885 he was awarded a Royal Scholarship; in 1886, the Murchison Prize in Geology; in 1887, the Tyndall Prize in Physics; and the Frank Hatton and Departmental Prizes in Chemistry in 1888, taking his Associateship in Chemistry, with special distinction, at the close of his course. During his studentship he threw himself with characteristic ardour and enthusiasm into the social life of the place, and took a leading part in all the College Societies, especially of the Union, of which he was the first chairman, and of the College Parliament, of which he was for a time Speaker. These positions not only



offered him opportunities for the exercise of much influence for good among the students, but afforded him occasion for the cultivation of his remarkable gift of clear and forcible exposition, thereby, no doubt, contributing to his subsequent success as a lecturer.

At the close of his student-career Mr. Rodger was disposed, for a time, to attach himself to biology, for which study he had always much sympathy. He soon discovered, however, where his real strength lay, and entering the chemical laboratory he devoted himself to research, working in conjunction with the writer of this notice. His first essay in investigation was a critical inquiry into the validity of Potilizin's 'law' of the mutual displacement of chlorine by bromine, the results of which were published in the Proceedings of the Society for 1888. The subject was of some little importance in relation to Berthelot's 'law of maximum work.' Potilizin's law states that if  $A$  be the atomic weight of a metal,  $p$  the percentage of chlorine displaced from its chloride, when this is heated with an equivalent quantity of bromine in a vacuous tube, and  $E$  its valency, then  $\frac{A}{pE^2} = \text{const.}$  Experiments

made with the chlorides of sodium, potassium, strontium, barium, and lead showed that the 'law' was altogether invalid, and was only very approximately fulfilled in the case of silver chloride. This paper was followed by a more ambitious, and, as it proved, a far more arduous piece of work on thiophosphoryl fluoride, a spontaneously inflammable gas discovered in the laboratory of the Royal College of Science, which was at that period occupied with the study of various fluorine compounds. The complete paper appeared in the Transactions of the Society in 1889.

During the next four years Mr. Rodger was almost exclusively engaged upon an inquiry concerning the relation between the viscosity, or internal friction, of liquids and their chemical nature. This investigation was part of the general question of the interdependence of the chemical and physical properties of substances which has occupied the attention of many workers from the time of Kopp downwards. It involved the accurate measurement of the internal friction of a large number of liquids of various types over comparatively wide ranges of temperature, and necessitated the preparation, with a scrupulous regard to purity, of a great variety of substances. For work of this kind, demanding knowledge, judgment, patience, manipulative skill, and a high ideal of accuracy, Mr. Rodger was particularly well adapted. The memoir when presented to the Royal Society was made the Bakerian Lecture for the year, and, by permission of the Council, it was arranged that Mr. Rodger, although not a Fellow, should deliver the Lecture. He was thus the youngest of all the Bakerian Lecturers from the time of Peter Woulff, the first in the series, whose memory mainly lives in

connection with the piece of chemical apparatus which bears his name. Mr. Rodger's powers of exposition were somewhat severely tried by this ordeal, but he discharged his task admirably, giving, in the necessarily limited time at his disposal, a remarkably well-balanced summary of a complicated investigation, dealing with many novel points in methods of observation, and in the reduction, treatment, and discussion of results. It may be claimed for this work that it has added considerably to our knowledge of the internal friction of liquids, more especially in relation to temperature, and that it has served to establish the fact of the intimate connection which exists between this particular physical property and the chemical nature of molecules. The results of the inquiry were published in the *Philosophical Transactions* for 1894. They were followed by a second paper, under the same title, which dealt more particularly with the ethers and esters, and was more immediately concerned with the profound effect of oxygen on viscosity, depending upon its mode of combination (*Phil. Trans.*, 189, 71, 1897). A third paper, on the "Relation between the Solubility of a Gas and the Viscosity of its Solvent," appears in these *Transactions* for 1894. A fourth paper, "On the Viscosity of Mixtures of Miscible Liquids," was also communicated to this Society, and was published in the *Transactions* for 1897.

Mr. Rodger's knowledge of the special field of inquiry to which he now elected to devote himself, combined with the power and ability he displayed as a teacher, induced "My Lords" to sanction his appointment as Lecturer on Chemical Physics in the Royal College of Science, and, until prostrated by illness, he annually gave a course of lectures on this subject during the summer term to the senior students in the chemical laboratory, which did much to popularise the study of this important and rapidly growing branch of science at South Kensington. He was also gradually gaining a position of authority as a writer on subjects connected with physical chemistry, as shown by his many articles and *critiques* contributed to *Nature* and to *Science Progress*. In 1894, he was promoted to one of the Senior Demonstratorships, and was placed in charge of one of the main chemical laboratories. This position, involving the superintendence of a large number of students, left him but little opportunity for research work during a great portion of the session. He was, however, too deeply imbued with the spirit of the true investigator to be readily daunted. He associated himself with the more promising of the senior students, to whom he communicated some part of his own zeal and enthusiasm in original work, one outcome of which is seen in the short paper published in conjunction with Mr. J. S. S. Brame, "On the Optical Rotations of Methyl and Ethyl Tartrates," which has recently appeared in the *Transactions* (1898, p. 301).

Such time as he could snatch after official hours, or during the vacations, he also gave to experimental inquiry, often working far into the night. It was under these conditions that he produced, in conjunction with his friend, Mr. W. Watson, the remarkable memoir, "On the Magnetic Rotation of the Plane of Polarisation of Light in Liquids," which was published in the *Philosophical Transactions* for 1895. In this paper the authors gave the results of a series of careful determinations, in absolute measure, of the magnetic rotation of carbon disulphide and water at different temperatures. It was intended to be the first of a number of papers dealing with the effect of the chemical nature of liquids on this property, and its correlation with other physical properties, concerning which Mr. Rodger had collected a considerable amount of bibliographical material. Unfortunately, the hopes which were centred round this paper were not to be realised. At about this period he gave serious indications of the malady to which he eventually succumbed. There is little doubt now that the strenuous labours of this time greatly aggravated his complaint. Although of active bodily habits and fond of out-door sports, he was never constitutionally strong. In spite of repeated warnings and the frequent advice of friends, he could not be induced to lie fallow for a while. The constant drafts on his great store of nervous energy were plainly undermining his physical powers. During the winter of 1895 he was attacked by influenza, from which he only slowly recovered. This, indeed, was the beginning of the end. Shortly after his return to work in the January of 1896, he again broke down; his condition was at once seen to be most critical, and he was granted extended leave. Although at times he seemed to rally, and spoke cheerfully of the future, the insidious disease from which he suffered steadily gained ground, and for some months before his death it was but too painfully evident that his friends must relinquish all hope of his recovery. He died of phthisis on May 30th, 1897.

Mr. Rodger was elected into the Chemical Society in 1892, and so long as his health permitted he was a regular attendant at the meetings, frequently taking part in the discussions, especially on papers relating to chemical physics. His power and promise were quickly recognised by the general body of the Fellows, and especially by those who were entrusted with the management of the affairs of the Society. He was at times of great assistance to the Publication Committee as a referee on papers connected with his special lines of inquiry. He was most painstaking and conscientious in the discharge of what is often a most delicate and invidious duty, and his reports were invariably characterised by judgment and strict impartiality. Although a comparatively young Fellow, he was eventually placed on

the Committee itself, and was at the same time made a member of the Library Committee and of the Committee charged with the preparation of the Collective Index of the Society's Publications. He was elected on the Council in 1896, but died before his term of office had expired.

Mr. Rodger had a singularly amiable disposition and great charm of manner. He was very popular as a teacher, considerate and helpful to students, ever ready to share in their aspirations, and to sympathise with them in their ambitions. With his elders he was no less popular; they respected him for his ability, and admired him for his manly independence, and his frank, ingenuous, straightforward bearing. By the writer of this notice, his memory will be cherished as that of one of the most lovable characters that he has had the good fortune to know and to be intimately associated with. T. E. T.

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43	15* for "0·1293" read "0·1292."
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1045	5* " "4,807 6 8" read "0 4 0."

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